May 26, 2009

Nancy Wittenberg, Assistant Commissioner
New Jersey Department of Environmental Protection
401 E. State Street
P.O. Box 423
Trenton, NJ 08625

Memorandum

RE: Summary of Comments on "Final Report: Contribution of Particle Emissions from a Cement Facility to Outdoor Dust in Surrounding Community"

<u>Executive Summary</u>

On October 6, 2008, Paul J. Lioy, PhD, Zhi-Hua Fan, PhD, and Chang Ho Yu, PhD (Lioy et al.) submitted a document to the New Jersey Department of Environmental Protection --Division of Science and Research, titled *Final Report: Contribution of Particle Emissions from a Cement Facility to Outdoor Dust in the Surrounding Community* (the "study" or the "report"). The report provides a description of work conducted to assess the potential impacts of particulate emissions from the Holcim (US), Inc. (Holcim) facility (the "facility", formerly St. Lawrence Cement) in Camden, New Jersey on the nearby Waterfront South (WFS) neighborhood. ENVIRON International Corporation (ENVIRON) was retained by Holcim to review the report. This memo is the summary of ENVIRON's analysis. As set forth in detail herein, our review reveals that the data collected in the study cannot be reliably used to evaluate the potential contribution of fugitive particulates from the facility to outdoor dust in the WFS neighborhood.

As described in the report, the researchers compared samples of raw cement material (RCM) from the facility to dust samples collected in WFS in an effort to estimate Holcim's potential contribution to outdoor dusts in the neighborhood.

To assess the composition of dust in the area, two types of ambient samples were collected:

- Surface wipe samples, which are samples of dust that has deposited on various surfaces (e.g., tops of air conditioners, outdoor ledges/sills) in the vicinity of the facility; and

- Particle deposition samples, which are collected by placing collection devices at various outdoor locations over an extended period of time (21 to 31 days) and allowing particles to settle onto the collection devices.

In an effort to assess the potential contribution of the facility to outdoor dust, these dust samples and a sample of RCM were analyzed in the laboratory for a range of elements. As the elements within RCM are ubiquitous in ambient air from a number of natural and man-made sources, samples of dust were also collected at a background site, namely the Gloucester City Park, 1.4 miles upwind of the facility, to serve as a point of comparison. The data generated from the study were subject to various statistical tests and also used in an EPA model (Chemical Mass Balance or CMB) to evaluate the potential contribution of the facility to outdoor dust.

Based on our experience in dust collection and analysis methods and general knowledge of the composition of RCM and particulate matter in Camden, we have listed below key issues/concerns that we have identified regarding the study.

1. In order to make a comparison of individual elements in RCM and the collected dust, it is critical to accurately analyze the composition of the samples. RCM is comprised predominantly of silicon, calcium, aluminum and magnesium oxides, with an average silicon dioxide content of approximately 35%. The composition analysis presented in the study indicates RCM has less than 0.01% silicon. This discrepancy calls into question the analytical techniques used and the overall reliance on the elemental analysis, which is the foundation of the entire study.

2. In an attempt to evaluate the facility contribution to the dust collected in the deposition samplers, the CMB model was used in the study.[1] To produce accurate results, the model requires a characterization of the various sources that contribute particulates to ambient air. This characterization was not conducted for sources other than RCM and it is evident, as discussed above, that the elemental composition of RCM used in the study is incorrect. A discussion of issues associated with the CMB modeling is provided in the detailed comments, although the results of the CMB modeling are revealing enough. Contrary to expectations, the CMB model indicates that automotive emissions do not contribute to fine particulate dust in Camden and Gloucester City.[2] Since automotive sources are generally regarded as a significant contributor to fine particulates in highly trafficked areas like Camden, the CMB results are suspect and cannot be relied upon.

3. To the extent that a concern has been expressed about dust settling in the WFS neighborhood, the collection and analysis of surface wipes is a reasonable first step for the evaluation of any problem. Wipe samples were collected from 15 different locations as part of the study. Various statistical tests were done evaluating the dust loading (i.e., how much dust was found at various distances from the facility) and elemental composition (i.e., how do individual elements and ratios of different elements compare with the elemental composition of RCM) of the wipe samples. The results of these tests may be found in different parts of the report and indicated, "the dust mass collected by the surface wipe samples were not associated with the distance to the facility." Similarly, for individual elements such as calcium, which was found at relatively high concentrations in RCM, no statistically significant decrease was

---

[1] It should be noted that the study relies on tiny amounts of fine dust that infiltrated the particle deposition samplers for the CMB modeling, which was not the original intent and, as described below, does not represent settling particles.

[2] As will be discussed below, this model output is the result of inappropriately selected model input, i.e., source characterizations from a 1970s era study in Portland, OR.

observed with increasing distance from the facility. Thus, although the study fails to provide an overall conclusion based on the surface wipe analysis, it is evident that a facility impact is not discernible from the samples collected.

4. The remaining samples collected during the study were particle deposition samples, which, as described above, are collected by placing collection devices at various outdoor locations over an extended period of time (21 to 31 days) and allowing particles to collect on the sampling devices. The collection device used in the study may be visualized as a circular plate that collects airborne dust. The unique attribute of this particular device was the inclusion of a hood of diameter approximately 50% larger than the plate, placed less than 1 inch above the plate to protect the deposition plate from rain. While potentially effective in presenting a barrier to falling rain, the hood (which was an inverted funnel) would be equally effective in preventing dust from settling onto the plate. From an analysis of the particle size distribution of the collected material, it is evident that only the finest particles entered the device. The study was designed to collect large size particles (more than 10 micrometers in diameter) which were estimated to settle to the ground near the facility. However, due to inadequacies in the collection device, coarse particles were excluded, so any conclusions drawn from the CMB modeling are meaningless since the minor amounts of dust actually collected are not representative of the overall dust in the community. Approximately 99 percent of the dust collected consisted of particles less than 10 micrometers in diameter, a size range that the researchers estimated would not settle near the facility. Data from this unconventional sampling device cannot be used to provide any indication of settling dust in the neighborhood, and any dust collected cannot be considered representative of airborne particulates.

In conclusion, for the reasons described above, the data collected in the study cannot be reliably used to evaluate the contribution of fugitive particulates from the facility to outdoor dust in the WFS neighborhood. A more detailed discussion is provided below and divided into four sections that discuss sample collection, laboratory analysis, data analysis, and CMB modeling. A final section, titled "Materials Requested for Further Review", provides a list of additional data needed to further evaluate a number of the study findings.

I.   Sample Collection

According to the report, airborne dust was collected using a fabricated deposition device ("airborne" or "deposited" dust samples) from 12 locations in the vicinity of the facility during the first field campaign (Round 1) between July 5 and 26, 2007, and from 10 locations during the second field campaign (Round 2) between August 17 and September 17, 2007. In addition, surface dust samples were collected using wipes ("surface" dust samples) from 15 locations in the vicinity of the facility during the summer of 2007. Most of the airborne dust and surface dust samples were collected from locations in the WFS residential neighborhood located northeast of the facility. A one-time composite sample of the RCM pile was collected on an unspecified date during the summer of 2007. All of the samples were weighed, digested by the microwave oven-assisted digestion method, and analyzed for elements by inductively coupled plasma mass spectrometry (ICPMS). Five airborne dust samples from Round 2 and the RCM bulk sample were also analyzed by MVA Scientific Consultants for morphology by polarized light microscopy (PLM) analysis and for size distribution and elemental composition by scanning electron microscopy (SEM) and x-ray analysis. However, these results are not discussed in the report, and therefore cannot be evaluated. The following sections discuss

specific issues/concerns that have been identified in connection with the sampling devices, locations, and methodology used in the study.

A.   Sampling Device

There are a number of issues associated with the design of the sampling devices used in the study. As such, the dust collected in these devices is not representative of actual dusts in the WFS neighborhood. Accordingly, the data generated from these samples cannot be reliably used to evaluate, or reach any conclusions, regarding potential dust contributions from the facility.

Passive samplers, like the ones used in this study, are not considered accurate and are recommended only as a scoping method to identify deposition "hotspot" areas for investigation using another sampling method (EPA 2001). Ambient air sampling methods are considered most accurate for dry deposition sampling (EPA 2001). Ambient air samplers measure pollutant concentrations in air, from which deposition rates are calculated using deposition velocities. In addition, particulates collected on air filters can be sent to a laboratory for compositional analysis.

If passive deposition samplers are used, the 2001 EPA Atmospheric Deposition Handbook further recommends the collocation of dry and wet deposition samplers to provide a more complete understanding of deposition at a particular location. Actual deposition is made up of both dry and wet deposition, and, therefore, dry deposition sampling only provides a partial picture. Dry deposition sampling is prone to particle bounce-off and resuspension, which further contributes to the underestimation of actual deposition. The subject study does not explain why wet deposition was not measured or discuss the limitations of the passive dry deposition sampling method. In addition, because of the inaccuracies associated with passive dry deposition sampling and the particular sampling device used in the study, the associations between radial distance and dust loadings are called into question.

The dry deposition sampler used in the study is subject to design issues that may affect the total mass, as well as the size distribution, of particles collected on the filters. The samplers consisted of cellulose filters placed on a petri dish and a funnel -- mounted two centimeters above the dish -- to prevent rain infiltration (see Figure 1, below). The funnel on the sampler used in the study has the effect of restricting deposition of particles onto the collection filters. Lower-velocity and larger particles from all sources would be underrepresented on the collection filters. This sampler design does not appear to be based on any generally accepted sampling method.[3] The ASTM standard for dustfall collection and measurement (ASTM D1739-98) recommends the use of an open-topped cylinder equipped with a wider-opening windshield (see Figure 2, below) to simultaneously collect wet and dry deposition. The cylinder and windshield are then mounted on a pole such that the top of the container is two meters above ground. Whereas the ASTM-recommended sampler design uses a cylinder and wind

---

[3] The sampler used in the study appears to be loosely based on a device described in a 2004 Franssens et al. publication on a lead-zinc refinery. Although the study references the 2004 Franssens et al. publication as the basis for their sampler design, Franssens et al. places cellulose filters on a polyvinyl chloride (PVC) plate without any type of cover. Franssens et al. acknowledge that their 2004 study may be the first time that cellulose filters have been used as a dry deposition collection substrate and they include the caveat that "measured deposition rates will have to be considered as lower limits, due to possibilities of particles bouncing." The study has not addressed this concern about their sampler design

Figure 1
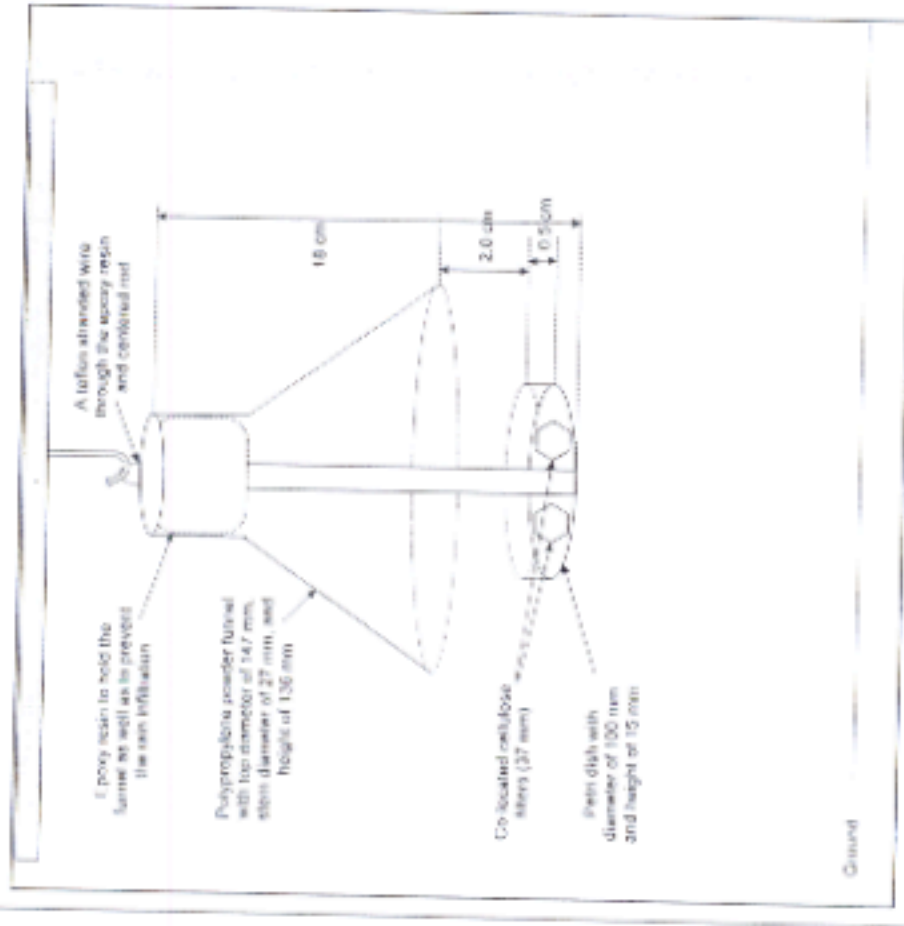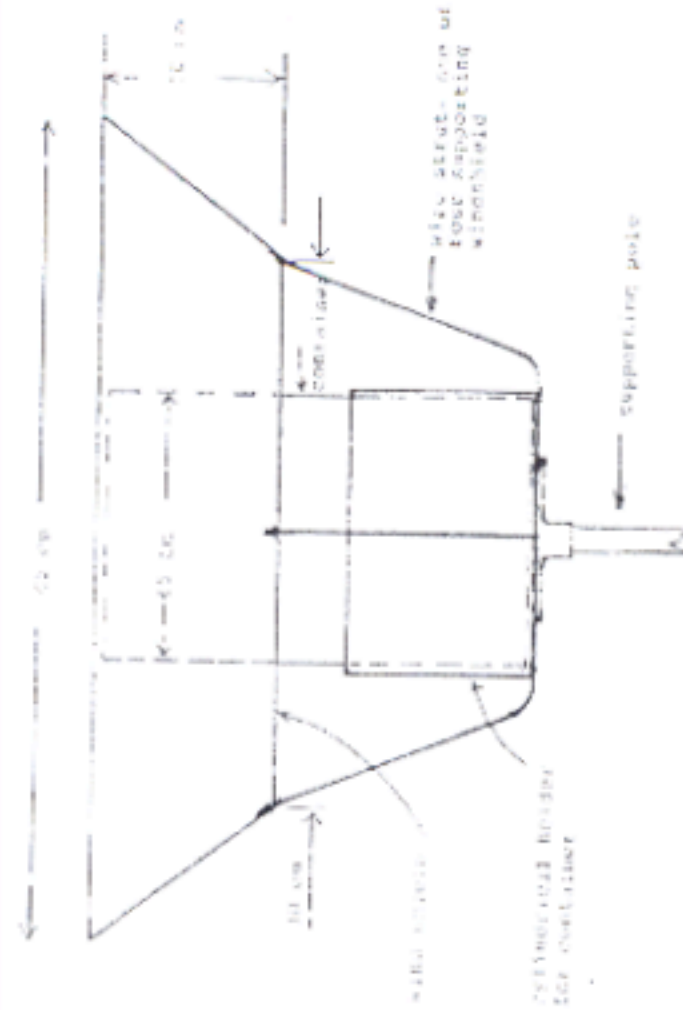Sampler used in the study (Lioy et al. 2008)

Figure 2
Sampler configuration described in ASTM D1739-98 (1998)

shield to reduce particle scavenging by strong winds, the petri dish only has a 15-mm rim and no wind shield.

The RCM and five airborne dust samples were analyzed for particle size distribution, which further illustrates the effects of the sampling device design. Table 5 in the report presents the size distribution results for only three "deposited" dust samples. Approximately 99 percent of the particles were less than 10 μm in diameter. This result is more a reflection of the sampling device than the nature of particulates in ambient air since larger particles would not reach the collection filter (because of the funnel) or would bounce off. As discussed in Section 2.1 of the report, the focus of the study was actually larger particles (greater than 10 μm) that were more likely to deposit in the vicinity of the facility, as indicated in Table 1 of the report. The size-selective design of the sampler and the potential loss of collected coarse particles from bouncing or wind scavenging resulted in the collection of particles that are not representative of the overall dust deposits in the Waterfront South (WFS) neighborhood. Elemental composition of dusts often varies with particle size, therefore, missing or underrepresented size ranges would change the elemental concentrations. Because the elemental concentrations form the basis of the percent estimation of RCM contribution to outdoor dusts, the study's conclusions are based on data that do not reflect the actual dusts in the neighborhood.

B.   Sampling Configuration and Location

Our review of the sampling configuration and locations revealed inconsistencies and potential sources of contamination associated with the dust/data collected during the study. Based on the location comments provided in Tables 2 and 3 of the report, the dry deposition samplers were sited near buildings or trees, which present barriers to deposition. Additionally, trees can act as both deposition surfaces and sources of particulates (e.g. pollen). Eight of the 12 locations in Round 1 and seven of the 10 locations in Round 2 appeared to have been sited near a building or a tree. Based on the sampler design (Figure 2), the photograph (Figure 3), and comments in Tables 2 and 3 of the report, it appears that some of these samplers were hung from trees or porches, which would affect the total particle deposition as well as the size distribution of particles depositing on the sampler. According to the ASTM D1739-98 dustfall standard, the sampling site should be "in an open area, free of structures higher than 1 m within a 20-m radius of the container stand." In ASTM D1739-98 and ASTM D5111-99, which provides guidelines for atmospheric deposition monitoring site selection, the recommended distance to any object greater than the height of the sampling device is at least twice the height of the object, so that no object is greater than 30 degrees from the horizontal. At minimum, the distance should be no more than the height of the object (see Figure 3, below). Based on the information provided in the study, where samplers were located next to buildings and trees (or possibly under them), the majority of the sampling locations did not meet these guidelines. As a result, the usefulness of making associations between dust loading or enrichment factors and radial distance is limited because interference from these overhead structures at some locations would have likely obstructed particle deposition. Sampling configuration and location undermine the study's conclusions that the mass of deposited dust and calcium concentrations in the deposited dust samples decrease with increasing radial distance from the facility because the researchers cannot account for the effects of surrounding structures and trees. Other errors in the study analysis, discussed later in this memorandum, further undermine the conclusions.

Figure 3
EPA's Recommended and Minimum
Acceptable Distance to Sampler
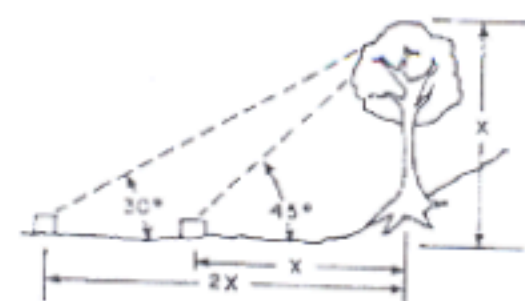
Source: EPA 2001.

The inconsistency of the deposition sampler height also introduces another variable which inhibits the study's attempt to correlate the distance from the facility to dust in the WCS neighborhood. According to the ASTM D1739-98 dustfall standard, studies have found that there is wide variability in the total concentration of particles subject to settling at heights of less than two meters. For this reason, the ASTM standard recommends a consistent sampling height of two meters. This recommendation is followed in the Franssens et al. publication on which the sampler design is based, but it does not appear to have been followed in this study. A sampler placed two meters above ground and one placed closer to ground level would be expected to collect different sizes and compositions of particles. For example, a sampler closer to ground level would likely collect more resuspended pavement or yard dust. The samplers in the study were placed on balconies, porches, trees, yards, etc., and were likely at different heights above the ground surface. The height variation raises questions about the study's associations between the enrichment factors and radial distances.

The sampler height variation poses additional concerns, including errors in the traveling distance calculations in Table 1 and the introduction of another variable in sample collection. The traveling distance calculations assume that particles travel from the top or middle of the RCM pile (9.0 or 4.5 m) to the ground. Because many of the dust collectors were apparently located well above ground level (balconies, ledges and sills, etc), the distances presented in Table 1 in the report may have little relevance to the design of the study.
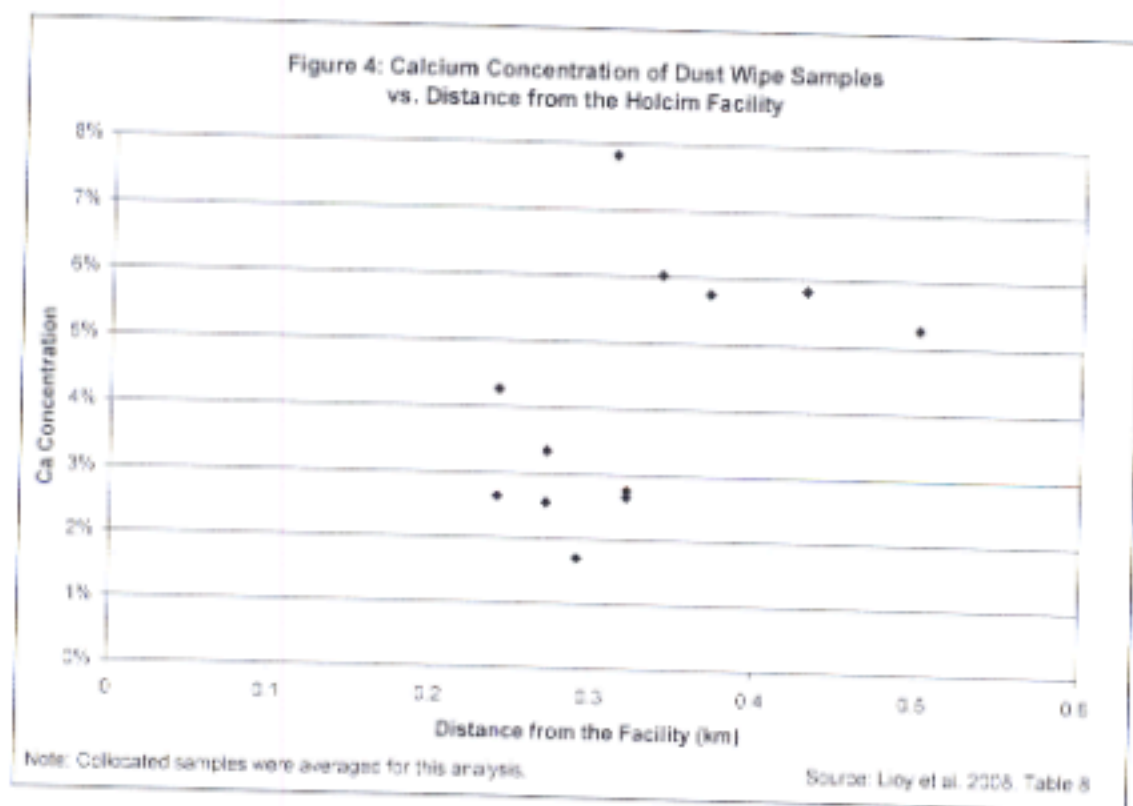
In addition, according to ASTM D1739-98 as well as an EPA guidance document for PM monitoring site selection, sampling locations should be placed at a distance from paved roads and parking lots because of exhaust and road dust. Even for a source-oriented middle-scale (100-500 m) sampling locations such as the locations in this study, the samplers should be located at least 20 meters from a tree and 50 meters from the nearest busy roadway (ASTM D1739-98, Watson et al. 2007). Based on the photographs and location maps provided in the study, it is not clear if the sampling locations were located a sufficient distance from roadways. Additionally, two locations in Round 1 were located in a parking lot, and it is unknown if the parking lot was active at the time. Samplers placed near roadways and parking lots would be expected to have higher dust loadings and different particle size distribution and elemental composition profiles.

Finally, the control sites were not selected in such a way to allow for consistent comparison to neighborhood sampling locations, which included residences, open spaces, and parking lots. According to the study, the prevailing wind directions are to the southwest or northwest in the

Camden area. EPA guidelines for atmospheric deposition sampling recommend a combination of upwind and downwind sampling locations (EPA 2001). The samplers used in the study were placed northeast and downwind of the facility, except for one location (No. 11) in Round 1 and two locations in Round 2 (No. 9 and 10). Unfortunately, Round 1's upwind sampler (No. 11) was lost. The two locations used in Round 2 (as well as the location of the missing No. 11), were near trees, which would have affected particle deposition, as discussed earlier. Although the proximity of the Delaware River west of the facility reduced the availability of upwind locations, the placement of samplers in upwind areas that are more similar to the WFS neighborhood and in southeast locations downwind of the facility would have improved spatial coverage. The difference in sampler siting in the control sites as compared to the WFS sites weakens the study conclusion that calcium concentrations decrease with increasing distance from the facility.

C.   Surface Wipe Samples

Based upon the information provided in the report, it appears that the surface wipe sample results do not indicate a facility impact in connection with dust in the WFS neighborhood. These surface wipe samples were the only samples of deposited material in the study that reflect overall cumulative deposition, taking into consideration natural conditions. Although the report acknowledges the lack of a facility impact, the analysis underlying this conclusion was not well described (for example, Figure 4 below could be used to demonstrate the lack of correlation of calcium concentrations with distance from the facility). Rather, the study researchers make a concerted effort to discount the results of the surface wipe samples, although the parallel deposited dust sampling did not receive the same level of critical review and scrutiny.

Figure 4: Calcium Concentration of Dust Wipe Samples vs. Distance from the Holcim Facility

Note: Collocated samples were averaged for this analysis.

Source: Lioy et al. 2008, Table 8

Flaws were also identified with the collection of the surface wipe samples that may have resulted in inaccurate mass and elemental concentration measurements. For example, surface wipe dust samples were collected from a metal drum bin, electrical boxes, air ducts,

air conditioners, and a vending machine, which typically have metal surfaces. Metal particles from these surfaces may have been inadvertently removed during the wipe sampling and included during the sample analysis. The report acknowledges that two samples were collected near deteriorating metal surfaces, which may have resulted in elevated metal loadings for those locations. The authors of the study also indicate that some of the surfaces were electrically charged (e.g. electrical boxes) and would be expected to attract more particles.

D.   Bulk Raw Cement Material (RCM) Samples

The one composite sample collected on-site may not be representative of the range of typical conditions on the RCM pile. As such, the elemental concentrations and enrichment factors derived from the RCM sample may not accurately reflect fugitive emissions from the pile.

The study researchers collected one composite sample (comprised of three subsamples) from the RCM pile located at the facility on one day. The study assumed that there was no variability in the particle size distribution and chemical composition of the RCM pile over time. However, recent precipitation, pile loading/unloading activities, and natural variation in the RCM composition could have resulted in different size distribution and chemical composition of these materials over the course of the study. For example, moistening of the pile after rainfall can cause cementatious binding and potentially larger particle sizes. Changing pile levels as a result of the addition and use of RCM may also affect the size distribution. Also, based on routine XRF testing of RCM delivered to the facility, the chemical composition of RCM varies. RCM typically averages approximately 35% silicon dioxide content, but can range from approximately 25% to 45%. The percentage of calcium oxide averages approximately 40%, but can range from approximately 25% to 40%. These variations could have been captured by collecting multiple samples at different time periods during the deposition sample collection period.

The study assumes that the composition of the RCM bulk sample reflects the composition of particulate emissions from the site. Particulate emissions from the site may arise from a number of sources and may have a different particle size distribution and elemental composition from the filtered bulk material sample.

E.   Other Regional Sources

The study considered the RCM pile as the only possible dust source; other possible regional and local sources of dust were not investigated and sampled, including road dust, vehicle exhaust, refinery emissions, and metal processing. The study found that the enrichment factors for lead and zinc were higher than the enrichment factors for RCM, and attributed increased levels of lead and zinc in ambient air to a metal treating facility and an iron workshop in the neighborhood. However, there was no further attempt to quantify the dust contributions from these metal processing facilities or any other facility in the area. This is one of the most significant flaws in the study and one that would certainly have an adverse impact on the validity of the study results. Enrichment factors, and associated issues, are discussed further in the Data Analysis section below.

F.   Other Sampling Issues

Very little information is provided in the report about the blank samples for this study. Field and lab blanks for the surface wipe samples are listed in Table 4 of the report (as averages only), but no blanks are reported for the dust deposition samples listed in Tables 2 and 3. Any blanks collected with the dust deposition samples should be reported in these tables. The text indicates that "Sample concentrations were field blank subtracted before data analysis." If this means that the concentrations in the field blanks were subtracted from the concentrations in the field samples reported in the later tables (e.g., Table 8), the concentrations in the field

blank should be reported. Information was also lacking on how non-detects were addressed in this process if an element was not detected in a field blank.

Similarly, documentation that is typically associated with a field sampling event, including sampling protocols, field notes, chains-of-custody, etc., was not available for review for the various samples collected. As a result, it is not possible to evaluate if the study followed proper handling procedures for retrieving samples.

II.   Laboratory Analysis

The failure of the study's laboratory analysis to detect silicon at levels that accurately reflect the composition of RCM (average silicon dioxide content of approximately 35%) draws into question the study's analytical techniques and the overall reliance on the elemental analysis. RCM is comprised predominately of silicon, calcium, aluminum, and magnesium oxides. Historical XRF data for RCM confirms this composition, with approximate average values as follows: 35% SiO_2, 40% CaO, 10% Al_2O_3, and 8% MgO. Silicon should have been a major component detected in the elemental analysis of RCM. However, very low levels of silicon were detected in the elemental analyses. It was detected at only 0.0017% in the RCM sample, and also at very low levels (<0.03%) in the airborne deposition samples. Meanwhile, calcium, aluminum, and magnesium were detected at 30%, 19%, and 14.6%, respectively. According to the laboratory procedures outlined in the study, the dust samples were digested by the microwave oven-assisted digestion method with concentrated nitric acid (EPA methods TO-3050a and 3052). According to EPA method TO-3052, samples with silicon dioxide (SiO_2) require concentrated nitric acid and hydrofluoric acid for proper digestion. Nitric acid alone will not sufficiently digest silicates, and can result in unreliable recoveries (EPA TO-3052, Sun et al. 2001). The study does not indicate that hydrofluoric acid was used in the digestion method. The use of nitric acid only could explain the very low levels of silicon detected. The omission of hydrofluoric acid also raises questions about whether elements bound in silicate structures were dissolved and accurately measured.

The report indicates that five dust samples and one RCM sample were analyzed by microscopy, but Table 5 of the report only includes three dust samples (two are missing). The particle size distribution for each sample is represented by a percentage for each of six size categories listed under the heading "Diameter Range (μm)". Most particles are not spherical and it is unclear if the sizes are reported as an aerodynamic diameter or as physical dimensions. The protocol used to classify the particles by size should be explained, but is lacking, in the report.

Background information on laboratory techniques and analysis has not yet been made available for review. For example, the MVA microscopic analysis reports, which are listed as appendices, are not included in the study report.

III.   Data Analysis

In addition to the issues identified with the sampling methodology and laboratory techniques used in the study, the data analysis presented in the report could not be fully understood or evaluated because the methods were not explained in adequate detail. It is apparent from the information provided, however, that there are inconsistencies in the tables and deficiencies in some of the statistical analyses in the report. These issues are discussed in detail in the following sections.

A.   Sample/Filter Selection

The report does not explain the procedure used to select the samples and filters used in the data analyses, and some of the information needed to assess the representativeness of these samples and filters is not provided. Four filters were placed in each airborne dust sampler, but the report (Tables 2 and 3) does not provide the mass measurements for the individual filters. The later tables (6 and 7) report mass measurements and other data collected from 28 individual filters, but it is not clear how these filters were selected. It appears that 16 of 52 filters collected in Round 1 were analyzed, and that 12 of 72 filters collected in Round 2 were analyzed. If they were reported, the mass measurements from all 124 filters could be used to assess the degree to which the 28 filters selected for additional analysis are representative of the complete set of filters. In addition, these mass measurements might be used to test for systematic differences in collection efficiency between samplers in the different sample locations.

B.   Independence of Collocated Samples

The process used to investigate the relationships between collocated samples should be described in greater detail. At a minimum, the number of independent samples used in each analysis should be provided. The tables in the report indicate that some of the filters selected for the elemental analysis were from the same sampler (e.g., D001A and D001B) and others were from collocated samplers (e.g., D001A, D001B, and D002A). The 16 filters reported in Table 6 (Round 1) were collected in 13 samplers at only 8 locations, and the 12 filters reported in Table 7 (Round 2) were collected in 10 samplers at 10 locations. Filters from the same or collocated samplers should not be treated as independent observations. It is unclear if the results from all of the filters from each location were averaged before analyzing the relationships with distance, or if some of the results were excluded from the analysis.

This concern also applies to the surface wipe samples. Table 8 in the report indicates that there are three pairs of collocated samples in the 18 surface wipe samples selected for elemental analysis. Table 4 of the report suggests that the collocated wipe samples were collected from the same surface or type of surface (although the sampled area differs greatly at some locations but not at others). Wipe samples collected from the same or similar surfaces at one location should not be treated as independent observations. A similar concern as that mentioned above about whether the samples were averaged or whether some samples were excluded exists here. It is also unclear from the report if the wipe samples at each location were collected on different dates.

The report does not specify which deposited dust samples were used in some of the analyses, so it is not clear whether data from the two sampling rounds have been combined. The deposited dust samples were not collected at the same locations in Rounds 1 and 2. Using data from both rounds together would provide a larger sample size (desirable for statistical analysis), but there may be systematic differences between the rounds. These potential differences should be evaluated before using the data from the two rounds together in the same analysis. The absence of control/background samples for Round 1 complicates this evaluation.

C.   Calculation and Reporting of Enrichment Factors and Ca/Fe Ratios

There are several inconsistencies in the report in connection with the study's calculation and reporting of enrichment factors and calcium/iron (Ca/Fe) ratios. First, the list of elements reported in Table 9 of the report differs from the lists reported in Tables 6-8, and the list in Table 8 is slightly different from the list in Tables 6 and 7. It appears that concentration data are available for at least 21 elements all together, but the same elements are not reported in each table. Titanium is missing from Table 8 even though the enrichment factors are based on Ti concentrations.

In addition, the concentrations of the elements in the reference material used to calculate the enrichment factor values in the report should be provided in one of the tables. The reference material used to calculate the enrichment factor values is identified as "Mason's crustal rock composition values (Rahn, 1976)." There are other references for calculating enrichment factors from dust samples and it is not clear why the researchers chose Mason's reference rock instead of, for example, Bowen's reference soil for their calculation.

D.   Relationship Between Dust Mass and Distance

As a general comment applicable to all the distance analyses conducted in the report, to conduct a statistical evaluation using the distance parameter, samples need to be collected at different radial distances from the site on a single transect. Since transect testing was not conducted, conclusions cannot be drawn from statistical analysis using the distance parameter. The report indicates that there is an inverse relationship between the mass of dust collected and distance from the facility. The Spearman rank correlation coefficient value presented in the report (-0.7697) appears to have been calculated using the average values for each of the 10 deposited dust sampling locations used in Round 2. Two of these 10 locations are identified in Table 3 as "control site (tree)" and are referred to as background locations elsewhere in the report. These two locations are apparently upwind of the RCM pile and should not be used to determine whether the mass of dust collected decreases with increasing distance downwind of the RCM pile. The p-value reported at the top of page 8 (0.0069) suggests that the rank relationship between dust mass and distance is highly significant. This p-value appears to have been calculated using a method (the Fisher R to Z transformation) that is not accurate for Spearman rank correlation tests involving small numbers of samples. The correct p-value for a rank correlation of -0.7697 based on 10 observations is between 0.02 and 0.05. Excluding the values from the two background locations changes the value of the Spearman coefficient from -0.7697 to -0.5476 and results in a p-value greater than 0.05. Thus, the statement that there is an inverse relationship between the mass of dust collected and distance from the facility is only supported by the rank correlation analysis if the two upwind background locations are included.

As another example of inconsistency and poor documentation, the report states that the minimum mass collected in the surface wipe samples was 1.71 mg. This value does not appear in Table 4; it may be associated with one of the field or lab blanks. The text indicates that no spatial pattern was observed in the mass values for the wipe samples, but it is not clear how this conclusion was reached. Thus, in order to evaluate these conclusions, it is necessary to know what patterns were considered and how they were evaluated. Similarly, it must be known if the relative elevations of the various wipe sampling locations were different enough to contribute to the differences in mass and loading. Without this information, these conclusions cannot be properly evaluated.

E.   Relationships Between Elemental Composition and Distance

The report suggests that the calcium concentration is a surrogate for the contribution of the facility's emissions to the deposited dust samples. An exponential relationship between calcium concentration and distance is illustrated in Figure 6 of the report and described in the text. However, the distances indicated in the figure do not generally match the distances shown in the tables, and when the distances are approximately equal, the calcium concentrations are generally not. The authors may have used data from both sampling rounds and may have averaged data collected at different locations to construct the figure and fit the curves. The relationship between the nine data points shown in the figure and the data in the tables should be explained in detail. Sampling from different rounds cannot be combined unless the potential for systematic differences is evaluated. The report should also

provide sufficient information on the curve-fitting procedure to allow an interested reader to re-construct and evaluate the models used in the report and to consider alternative models.

The report concludes that only calcium had a statistically significant negative association between concentration and distance to the facility. The details of the evaluation for the other elements are not provided. The Spearman rank correlation coefficient and p-value reported here for the calcium-distance relationship suggest that this evaluation was based on 11 paired values, but it is not clear which sample observations were used in this analysis or whether the observations were used without averaging the values from the collocated samplers. As noted above, inclusion of samples collected at upwind background locations in analyses of the relationships between distance and particle characteristics may be inappropriate. Although it may be a coincidence, the p-value reported for this relationship (0.0037) is identical to a value shown in the preceding paragraph; one of these may be a typo. Also, as explained above, p-values for Spearman rank correlations derived using the Fisher R to Z transformation are not accurate for tests involving small numbers of samples.

There appear to be errors/inconsistencies in reporting the elemental composition of the dusts. For example, levels of cadmium in some of the samples are discussed in the text, but Table 9 does not include enrichment factors for this element. The elements are grouped by their prevalence and the report indicates that the concentrations of silicon were "primarily below 100 ng/mg" in the deposited dust samples. However, Table 6 shows that the silicon concentration was greater than 100 ng/mg in 12 of the 16 Round 1 samples. The possibility of systematic differences in mass, particle size distribution, and composition between the two sampling rounds (including the apparent difference in silicon concentrations) should be investigated and discussed in the report. If significant differences between the two sampling rounds are identified, the data sets from the two rounds should not be combined without addressing these differences.

The tables that report the elemental concentrations and enrichment factors should be expanded to include all of the elements covered in the data set, and the reference concentrations used in the enrichment factor calculations should be provided. The report should also note that the sum of the elemental concentrations reported for the dust samples typically accounts for only a small fraction of the total mass of the sample, so the suggestion that aluminum, calcium, iron, magnesium, and zinc are the "most abundant elements" in the deposited dust samples may not be correct. The elemental concentration data provided in the tables could be used to investigate the possibility of systematic differences between the sampling rounds, common types of sampler locations (e.g., trees vs. front porches), and other factors that may contribute to the variation in dust composition. The only relationship of this type that is addressed in any detail in the report is between the calcium concentration and distance from the RCM pile.

The report states that "the corrosive action of urban rainwater (with pH of below 4.0 in many cases)" may be responsible for the elevated levels of cadmium and zinc observed in two wipe samples, but notes that the calcium loadings in these samples "were not significantly different from the loadings at other locations". If this statement of significance is based on statistical tests, the tests should be explained. The reference to increases in iron (as well as in cadmium and zinc) at the end of the paragraph should be explained or deleted.

F.   RCM Contributions to Outdoor Dust

The report states that, "We observed that the RCM contributions to outdoor dusts were lower as the radial distances are further from the cement facility (see Table 9)." This statement should refer to Table 10, not Table 9. The statistical significance of this observation should be tested and reported, preferably using averages for the collocated samplers, without combining

the data from the two sampling rounds, and using only the estimates that were produced with acceptable goodness-of-fit statistics. Without this analysis, the importance of the reported observation cannot be determined. Table 10 summarizes estimates of the RCM contribution to outdoor dusts derived by applying the CMB model to each of 28 dust samples, even though the report states that no more than 64 percent of the 28 samples provided acceptable goodness-of-fit statistics. At a minimum, the report should identify the samples for which the fit was acceptable and compile the statistics shown in Table 10 for those samples alone.

The Spearman rank correlation coefficient provided for the deposited dust samples in the last paragraph on page 9 appears to be inconsistent with the data in some of the tables. Attempts to reproduce the enrichment factor values in Table 9 using data from the other tables suggest that the enrichment factor for calcium may actually tend to increase with distance from the RCM pile. The report states, 'Except for calcium, other elements did not show an inverse relationship between enrichment factors and radial distance from the facility.' If the relationships for calcium are not statistically significant, it would be better to state that none of the elements showed a meaningful inverse relationship. The report should say whether a significant (positive) relationship was observed for any of the other elements.

Some of the values reported in Table 9 are not consistent with the earlier tables. The report indicates that enrichment factors for all of the elements analyzed in this study are provided in Table 9; but values for cadmium and antimony (which appear in other tables) do not appear in Table 9. The range of values reported for the Ca/Fe ratios in the deposited dust samples reported in the column headed 'Sampling Sites (<0.66 km)' indicates that the statistics in this column are derived from the 10 Round 2 samples without averaging the measurements from the collocated filters. As noted above, data obtained from filters from the same or collocated samplers should not be treated as independent observations in statistical calculations. An explanation as to why the Round 1 data were excluded from Table 9 should be provided in the report. Some of the values reported in Table 9 are clearly inconsistent with values in the other tables. For example, Table 9 indicates that the Ca/Fe ratio is 1.70 for both of the background deposited dust samples, but the concentrations in Table 7 indicate that the Ca/Fe ratio for sample D016-C is actually less than 1.64. The enrichment factor value for calcium also appears to be incorrect for one of the background samples; the correct average and range should probably be 8.30 and 7.18 to 9.43 (not 8.02 and 7.18 to 8.86 as shown in Table 9). Other values in Table 9 may also be erroneous or inconsistent with the earlier tables. The enrichment factor values cannot be checked easily because the concentrations in the reference material are not provided in the report.

IV.   CMB Modeling Analysis

The study used the United States Environmental Protection Agency's (USEPA) Chemical Mass Balance (CMB) model to determine Holcim's contribution to deposited dusts in the WFS neighborhood of Camden. CMB is a receptor model that apportions receptor concentrations into chemically distinct source types based upon source profiles provided by the user. The researchers developed receptor profiles for input into CMB using the chemical speciation data obtained from the deposited dust samples collected by the researchers in 2007. Source profiles were developed from the RCM collected from the Holcim facility as well as from other published data sources, including the Portland Aerosol Characterization Study (PACS). There are several issues with the researchers' application of the CMB model as well as their selection of source profile and receptor data. These issues are discussed in further detail below.

A. Applicability of Portland Aerosol Characterization Study Data

According to the report, the researchers used data from the PACS to derive chemical profiles for the majority of the source categories considered for the CMB model. The PACS dataset includes chemical speciation data for six source categories that were determined to contribute to urban aerosols in Portland in the late 1970s: (1) marine aerosol; (2) urban dust; (3) automobile exhaust from vehicles using leaded gasoline; (4) residual oil combustion (e.g., heavy fuel oils); (5) aluminum production; and (6) ferromanganese furnaces.

Since the PACS dataset was compiled to represent major emission sources in Portland in the late 1970s, there are several issues associated with the application of this dataset to deposited dust samples collected in Camden in 2007. Primarily, the six PACS source categories may not be representative of the types of emission sources that contribute to dustfall in Camden. For example, the Camden area has a number of industrial sources including waste incinerators, refineries, and metal treatment facilities. These industries may be a significant source of dust and may not be adequately characterized by the PACS. If so, the PACS data would not be sufficient to allow CMB to accurately apportion the deposited dust concentrations into source categories.

Additionally, geological differences between Portland and Camden may contribute to discrepancies in the chemical profiles of source categories such as urban dust. Regional differences in fuel and other industrial raw materials may also affect the chemical profiles of source categories such as residual oil combustion, aluminum production, and ferromanganese furnaces. In addition to these regional factors, the time period in which the PACS data was collected is problematic. Since tetra-ethyl lead was historically used as an anti-knock agent in gasoline, lead is the primary chemical marker of 1970s era automotive exhaust. Conversely, since leaded gasoline is no longer sold in the US, lead is not an appropriate chemical marker of present-day automotive exhaust. The CMB formatted PACS dataset only included the chemical markers of leaded auto exhaust (Watson 1976). Thus, there are significant concerns with the study's application of the PACS automotive data to dustfall samples collected in Camden in 2007. As discussed in the next section, this problem with the automotive source profile may have prevented CMB from recognizing automobile emissions as a contributor to particulate matter in Camden.

The above-stated issues could have a substantial impact on the source contributions predicted by the CMB model. In the absence of representative source categories and chemical profiles, the model will attempt to apportion dust across the input source categories, regardless of whether those categories accurately reflect dust sources in Camden. This type of force fitting would significantly impact model results.

B. Discrepancies between Model Prediction and Known Data

There are several discrepancies between the report's estimated source contributions (Figure 8 in the report) and known data. As discussed above, the CMB results suggest that the deposition samples collected in Camden and Gloucester City do not show any contribution from automotive emissions. Since automotive sources are generally regarded as a significant contributor to fine particulates, especially in highly trafficked areas like Camden, these results are highly suspect. Again, this discrepancy is likely due to problems with the chemical profile of the automotive source category, as described above.

C. Completeness of Chemical Speciation Data for Input into CMB

According to the report, the RCM and deposition samples collected during the outdoor dust study in Camden were analyzed only for metallic elements and not for ions (e.g., nitrate, sulfate, ammonium, etc.) or carbon. The Protocol for Applying and Validating the CMB Model for $PM_{2.5}$ and VOC (CMB Protocol) states that receptor data must include at least those

chemical species in the source profiles that allow unique source categories to be identified (Watson 2004). In order to accomplish this, the CMB Protocol states that "elements, ions, and carbon are the minimal needs for PM apportionment (Watson 2004)." Thus, it appears that the deposition and RCM sample data falls short of the minimum data requirements for use in a CMB model. Further, since carbon, nitrate, sulfate, and ammonium are major chemical components of $PM_{2.5}$ and PM_{10} in urban areas (Watson 2004), information on these chemical species is necessary to accurately determine contributions from various emission source categories. $PM_{2.5}$ speciation data collected from an ambient air monitoring station in Camden indicates that ammonium, nitrate, sulfate, elemental carbon, and organic carbon constitute nearly 80% of local $PM_{2.5}$ by mass (NJDEP 2005).[4] The absence of quantitative information on the carbon and ion content of the RCM and deposition samples may have prevented CMB from accurately differentiating between unique source categories and may lead to inappropriate contribution estimates, since the data on collected dust is incomplete.

D. Issues Associated with the Application of CMB to Quantify Impacts from a Single Facility

In developing source profiles for input into the CMB model, emission sources with similar chemical characteristics are typically grouped into representative source categories (i.e., marine aerosols, automotive emissions, etc.). Thus, the study's use of CMB to identify potential impacts from a single facility is not only unusual but likely problematic. CMB may not be able to distinguish Holcim's contribution from other similar sources that would typically be grouped into a single source category. Since the study did not include a detailed inventory of emission sources in the Camden area, it is quite possible that similar sources exist and have not been adequately characterized. Thus, the 'cement' source could actually represent a number of sources, in addition to Holcim, that emit material that is chemically similar to the RCM. This would cause the study researchers to attribute all cement-like emissions to Holcim, thus, over-predicting the facility's potential contribution to dust in the Camden area. This may be evidenced by the fact that the CMB model estimates that the study's background dust samples were comprised of up to 9% cement (i.e., RCM-like material). Since the background deposition samplers were located approximately two kilometers upwind of the Holcim facility, it is unlikely that Holcim contributed to dust at these locations. Therefore, the cement signature at these background locations was likely caused by other emission sources with chemical profiles similar to that of the RCM material.

Additionally, in order to characterize variability within a given source category, statistical analyses are typically conducted on a number of data points within the category. Since only a single RCM sample was collected in the study, the researchers assumed a default uncertainty of 10%. Further evaluation is needed to determine if this 10% adequately represents variability within the cement source category in the Camden area.

E. Potential Collinearity of Source Categories

In order for the CMB model to accurately differentiate between source categories, the source profiles for each category must be sufficiently different from one another. Similar or collinear source profiles could introduce a high degree of uncertainty (Watson 2004). The report does not discuss potential collinearity of the source profiles used as input data for the CMB model. It may be necessary to obtain additional information to confirm that the source profiles used for categories such as urban dust, geological components, and RCM are in fact independent of one another.

---

[4] The percent composition of local $PM_{2.5}$ by mass was calculated from average annual concentrations at the Camden Laboratory monitoring station in 2005.

F. Suitability of Deposition vs. Air Sampling Data

CMB is typically used to evaluate the types of potential emission sources that contribute to airborne PM in a given area or region. As such, researchers generally begin this type of analysis by collecting airborne PM samples (and not deposited or surface dust samples) in the region of interest in accordance with the Guidelines for PM-10 Sampling and Analysis Applicable to Receptor Modeling (USEPA 1994). Chemical speciation data for these air samples may then be input into the CMB model as receptor data. Conversely, according to the description provided in the report, the researchers collected dry deposition samples, and used the chemical speciation data from these samples as receptor data in the CMB model. Since deposition samples are not typically used to derive receptor data for CMB, the model results may be of limited utility, particularly when considered with source data from air samples, as collected during the PACS.

While surface dust samples are also not typically used to derive receptor data for CMB, more information is needed to evaluate if the study's exclusion of the surface dust samples was appropriate considering the researchers' inclusion of the deposition samples. The report states that, "Due to the high variability of elemental concentrations in surface dust samples (e.g., %Diff = 65 ± 37 % for 3 collocated duplicates), only dust deposition samples (N = 28) were used in the CMB model." The %Diff value cited here does not appear in the tables. Additional information is needed to evaluate if the study's exclusion of these samples is statistically sound.

G. CMB vs. Other Models

The CMB model is one of several air quality models that may be used to estimate potential impacts from known emission sources. Receptor models, such as CMB, UNMIX, and the Positive Matrix Factorization (PMF) model, use the chemical and physical characteristics of particles measured at emissions sources and receptors to quantify source contributions to receptor concentrations. CMB apportions receptor concentrations to chemically distinct source types depending upon source profile data input by the user, while UNMIX and PMF internally generate source profiles from ambient data. Alternatively, dispersion models, such as AERMOD, use pollutant emission rates and meteorological transport to estimate source contributions to receptor concentrations (Watson 2004, USEPA 2008). The report does not include a discussion of the criteria used to select CMB vs. other receptor or dispersion models. Additional information on this topic may be necessary to fully evaluate the researchers' source apportionment analysis.

H. Model Performance Measures and Validation

The CMB model uses several parameters to measure model performance, including R-square (R^2), chi-square (χ^2), and percent mass (%Mass).[5] The CMB Protocol suggests that R^2 be greater than 0.8, χ^2 be less than 4.0, and %Mass be between 80% and 120% (Watson 2004). The report indicates that these goodness-of-fit statistics were within the acceptable range for no more than 64 percent of the 28 samples. This suggests that the CMB modeling provided reliable results for at most 18 of the 28 samples. The goodness-of-fit statistics for all 28 samples should be provided so the samples with acceptable values can be identified and the others can be excluded from the later analyses.

Lastly, the CMB Protocol recommends conducting a formal validation of model results using other data analyses and source assessment methods. For example, the CMB Protocol
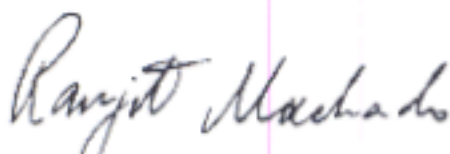
---

[5] R^2 is defined as the variance in receptor concentrations that is explained by the calculated species concentrations, while χ^2 considers both the variance in receptor concentrations as well as uncertainties in the calculated species concentrations. Percent mass is the ratio of total model-calculated source contribution to the measured mass (Watson 2004)

suggests that "both a dispersion model and a receptor model be used in a collaborative manner to perform an apportionment (Watson 2004)." The report does not describe the use of validation procedures to confirm the CMB model results. If such analyses have been conducted, a detailed description should be provided.

V.   Conclusion

In its attempt to assess the contribution of the Holcim facility to outdoor dust, the study contains several flaws that render the study incomplete and the conclusions essentially unreliable. Issues were identified with each step of the evaluation, from the sample collection, to the laboratory analysis, to the data analysis, to the modeling effort. Inadequacies in any one of these steps could adversely affect the study outcome, but the fact that each subsequent step of the analysis builds on flawed information makes the study unusable for the evaluation of a facility impact on outdoor dust in the WFS neighborhood.

Ranjit J. Machado, PE
Principal

VI.   Materials Requested for Further Review

Materials Pertaining to Data Collection
- Quality assurance plan
- SOP for all sampling activities (dry deposition, surface wipe, raw cement)
- Previous studies using the dry deposition sampler and comparison to other deposition samplers that conform to ASTM standards
- Sample log sheets and field books
- Meteorological data for sampling period
- Photographs of raw cement pile collection location
- Photographs of surface wipe locations with sample location no.
- Photographs of locations of deposition samplers with sample location no.
- Height of deposition sampler from the ground
- Criteria for selecting sampling locations
- Placement of collocated samplers

Materials Pertaining to Laboratory analysis
- SOP for laboratory procedures
  - Weighing procedures
  - Elemental analysis
    - Microwave digestion - EPA methods TO-3050a and 3052
    - Inductively coupled plasma mass spectrometry (ICPMS)
  - Microscopic analyses by MVA
- Laboratory reports
- Locations and results of field blanks
- Results of lab blanks and lab spikes
- Detection limits
- Appendices
  1. MVA Report for Microscopical analysis of particles on filters: D001-A, D005-A
  2. MVA Report for Microscopical analysis of particles on filters: D003-B, D018-C, D017-D
  3. MVA Report for Microscopical analysis of RCM <38μm

Material Pertaining to Data Analysis
- Particle size distribution for DO18-C and DO17-D (missing from Table 5)
- Elemental loading results for all surface wipe samples (should be two per location)
- Measured weight for all dust deposition, surface dust samples (not just averages)
- Dust deposition sample results (2nd field campaign) for uncovered sampler at locations No. 4 and 8
- Which sample locations (Location 1, 2, 3, 4, and 8) correspond to which sample number (D001-A, D005-A, D003-B, D-018-C, D017-D)
- Deposition dust samples used in Spearman correlation (why N > number of locations)

Materials Pertaining to CMB Modeling
- CMB inputs and modeling files
- Model performance measures, including (R^2), chi-square (χ^2), and percent mass (%Mass), for deposition sample