

**A COMPARISON OF EMISSIONS FROM THE
LAFARGE BROOKFIELD FACILITY in NOVA SCOTIA**

A review of stack testing data 2017 - 2020

A Report prepared for
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EXECUTIVE SUMMARY

As part of Lafarge's efforts to reduce greenhouse gas emissions they have been moving to reduce their reliance on coal in their cement kilns across Canada. One fuel replacement for coal is scrap tires which are anticipated to reduce greenhouse gas emissions by roughly 30% for every tonne of coal replaced. As a secondary benefit, NOx emissions are estimated to be reduced by 10-15% at that replacement level. Waste materials can provide energy to a cement kiln; however, there are concerns that such changes can influence other emissions from the process. Working with researchers and Nova Scotia Environment [NSE], Lafarge's Brookfield facility embarked upon a low carbon fuels strategy after approval was granted in 2017. That permission included requirements to undertake extensive testing of the stack emissions from the facility using protocols approved by NSE.

Monitoring stack emissions is accomplished in various ways: continuous monitoring of typical gaseous components such as sulphur dioxide, oxides of nitrogen, carbon monoxide and oxygen as well as opacity; periodic sampling of dust, metals, organic compounds (semi-volatile [SVOC] and two categories of volatile compounds), and chlorine compounds. The continuous monitoring data is typically averaged over a specified period and the variation in the results can be assessed to determine operational status. Periodic sampling requires extracting a minimum volume of the stack gases and collecting the target species in specially designed capture systems. For regulatory testing periodic sampling is repeated three times for any specific test series. The intent of repeatedly withdrawing samples is to ensure that any variability in the emissions is identified. To assess performance against regulatory standards, NSE requires that the sampling protocols meet the quality assurance/quality control standards set out in the methods and, if acceptable, the results are averaged and compared to the prescribed limits.

In addition to ensuring that any changes in operations at Brookfield did not cause excessive emissions, testing was designed to allow emissions to be compared for different fuel feeds. Typically, facility operation with the original fuel mix is referred to as Baseline operations, and testing was conducted in 2017 and 2019 under these conditions. Specific sampling were conducted during the use of low carbon fuels, [LCF], later in 2019 and again in 2020. These test results are the basis of the evaluation discussed in this report.

Even though testing was undertaken to ascertain emissions under both Baseline and LCF operating conditions, many factors can affect the emission profile. Since the process uses feed stocks mined from local quarries, it is not unusual to have the chemical composition of these materials vary. Such variations could lead to differences in emissions. Even the coal used as a fuel can have a varying chemical composition over time as the coal comes from different seams in the mine. Process conditions can alter emissions, particularly if those changes affect the performance of emission control systems such as the electrostatic precipitator [ESP] used to control dust emissions from the stack.

Another source of variation is the precision of the sampling methods. Precision is influenced by random error inadvertently entering the measurement process from the sample collection, or sample recovery, or sample analysis. When periodic sampling methods were developed by the USEPA they required simultaneously sampling using multiple sampling systems to ascertain if the variability in the result produced was low enough to ensure reliable results. That variability, expressed as the Relative Standard Deviation, can vary with

the concentration present in the stack being measured, but is not reflected in the any testing results typically provided to the regulatory agency.

The potential for variability in the testing results implies that it is insufficient to merely compare the average result for different testing campaigns. This assessment reviewed the stack sampling reports, recalculated all the emission concentration data for each parameter and each test and used that data in a statistical software package to compare the means of two independent groups to determine whether there is statistical evidence that the associated population means are significantly different. This is known as the Independent Samples t Test. Using this technique, it possible to ascertain if the observed differences occur by chance, or if they reflect a meaningful difference between the results.

The next step used in this evaluation was to determine if sampling method precision contributed to the identified differences. Using measured variability for test methods, it is possible, based upon the results of the ReMAP study, to determine what range of future measurements might result from the average concentration in the stack. Details of this approach are provided in the report. Those results that were statistically significant, but within the range of method precision, were concluded to show little difference between the test series.

Having defined that there was a meaningful difference, the results were be examined to find possible reasons for the differences. When attempting to explain results, the literature provides observations and reasons for variations found in other similar operations. A major source of information on cement kiln performance is the European Commission Best Available Technology report for the cement, lime, and magnesium oxide industry referenced elsewhere in this report. While not directly applicable to every site, trends noted in that document are useful for describing broad responses in emission data.

With four test series: Baseline 2017; Baseline 2019; LCF 2019; and LCF 2020 comparisons between each series could be conducted. A fifth series, the combined results of the Baseline testing series, was also created. Comparing each to the others, the list of 8 comparisons was completed for the metals:

Baseline 2017 to: Baseline 2019; to LCF 2019; to LCF 2020
Baseline 2019 to: LCF 2019; to LCF 2020
LCF 2019 to: LCF 2020; and to the combined Baseline
LCF 2020 to: the combined Baseline

For organics, the LCF 2019 SVOC data was not used for comparisons, and there were no data for VOCs for the LCF 2020 testing. This reduced the number of comparisons for the organics to 4 for each group.

Stack sampling requirements identified 222 possible elements or compounds that should be monitored, at least for the 2017 testing. That list was revised with the permission of NSE for later testing. This study compared the results for 196 elements or compounds excluding duplicate VOC results obtained using different test methods, and those compounds removed after the first test series.

The results of the statistical comparison of means tests identified that 59 of the 196 species measured during the various tests produced significant statistics. The species identified were distributed over the various test comparisons. The maximum number of differences identified in a single comparison was 29, the minimum was 11. The edited metals list from 2019 LCF produced between 5 and 16 significant statistics when compared to other tests. The SVOC from 2020 LCF produced 2 significant statistics when compared to the 2019 Baseline and the 2020 LCF series, and 12 significant statistics when compared 2019 Baseline was compared to the 2020 LCF data. VOC comparisons identified 6 compounds from the 2019 LCF testing that produced significant differences with Baseline tests.

For the combustion gases the comparisons showed that while there appeared to some differences in the averages, when the combined Baseline data was compared to the 2019 LCF averages, neither the CO or the NO_x produced t-statistics that were significant suggesting that there was no statistically significant difference between CO or NO_x results for the test series. The combined Baseline comparison to the SO₂ from the 2019 LCF test did produce a t-statistic that was significant suggesting that there was a difference between the means. The 2019 LCF SO₂ mean was lower than the combined Baseline mean. The reason for the lower concentration could be related to the low carbon fuel, or changes in the amount of sulphur in the raw meal. Ammonium was another gas sampled. The only comparison that produced a significant t-statistic was the comparison of the Baseline tests, 2017 vs 2019, even though the geometric mean for the 2020 series looks low. That was driven by a low value and a high value so there was a large variance in the result which reduced the significance of the t-statistic. The literature suggests that ammonium emissions are related mainly to the raw meal, suggesting that the chemical constituents of the feed change. Lastly, a comparison of the THC values was conducted for the 2017 and 2019 test series. The combined Baseline series were identified as producing a significant t-statistic when compared to the 2019 LCF results. The 2017 test series had a wide range of values compared to the narrow range for the other two tests and this reduced the significance to 0.038, still less than 0.05 but there is a 1 in 26 chance that this result could be erroneous. There was no difference between the 2019 values indicating that it is unlikely that low carbon fuel use would change THC emissions.

Particulate matter emissions were compared both with the full data set and with the suspect test removed from the 2019 LCF series. The change had no effect on the significance of the t-statistics, in both cases the 2019 LCF series produced a significant value when compared to the 2017 Baseline and the combined Baseline series. There was no difference between the 2020 series and the Baseline series, suggesting that the use of the LCF did not influence the emission results. When the 2019 LCF data was assessed with respect to measurement variability it was determined that the either of the 2017 or 2019 results could have been in the range expected from measurement precision. This suggests that the statistical findings were not environmentally significant.

The list of metallic elements identified for testing numbered 32. All were included in the independent means t-tests that were completed for the 8 combinations outlined previously. The 2017 Baseline series was missing 4 elements they had not been included in the analytical results. Approximately 25% of the comparisons produced t-statistics that were significant. For the balance of the comparisons, there were no significant differences found. Even though significant t-statistics were found by the comparisons they did not occur for all elements on all comparisons.

Eight elements produced no significant differences in mean concentrations regardless of the fuel used:

Chromium, Copper, Lead, Lithium, Nickel, Silicon, Thallium, and Vanadium,

A second group of elements were determined to show no changes in concentrations because in most cases the laboratory reported the results as being below the detection limit. Substituting the DL for these missing data created misleading mean difference statistics. When the data, with the substitution, is used for the means comparisons, it was found that the differences simply tracked the changes in the detection limits over the duration of the project. The individual elements are discussed in the text with explanations about the detection limits. The seven elements were:

Antimony, Beryllium, Bismuth, Cadmium, Phosphorus, Tellurium and Zinc

The remaining elements were assessed to determine whether normal sampling variability was a factor in the identified differences. If all the results overlapped using the ReMAP approach, method precision can be assumed to account for the differences. It was concluded that the use of low carbon fuels had no effect on emissions of these 7 elements:

Mercury, Arsenic, Cobalt, Manganese, Molybdenum, Selenium, and Silver

Some elements could not be assessed using the ReMAP methodology because the values recorded in the tests were outside the range of concentrations used to develop the ReMAP statistics. However, it was concluded that the data did not support a conclusion that fuel changes influenced the emissions of:

Aluminum and Iron.

Two other major constituents produced significant statistics, but high blank train levels were identified for these elements. Typically, blank train concentrations are a small fraction of the sampled values, but in the case of these metals the sample results are similar in magnitude to the blanks. This result, and the finding that the baseline and LCF series were similar, suggests that there is no meaningful difference from the use of different fuels for:

Magnesium and Sodium

A correlation between TSP emissions and the emissions of two elements that also are constituents of the raw meal suggest that there may be factors other than different fuels influencing the statistics for comparisons of:

Calcium and Strontium

The statistics and comparisons produced for:

Barium, Boron, Tin, and Titanium.

are not as easily explained. There are differences in the means, and method precision does not explain the differences.

Barium results were much lower for 2020 LCF series and that series could be an outlier in the data set. The other series showed no significant differences suggesting no influence related to fuel use.

Boron results for both 2019 series were dominated by BDL values reported from the laboratory and the substitution used for this study leads to inappropriate conclusions related to these tests. The Blank train in 2020 had similar levels in the HF digest indicating that laboratory procedures might influence emission levels. The 2017 Baseline and 2020 LCF test series were not statistically different suggesting that fuel changes are unlikely to influence boron emissions.

Tin emissions were lowest for the 2019 LCF series, and the means differences were identified for each comparison of 2019 LCF to the other tests. Also significant were the 2019 Baseline to 2020 LCF results. The ReMAP check of the effects of method precision identified that the 2019 LCF results did not overlap with the other results, and the 2020 LCF was at the low end of the Baseline test range. The data would indicate that LCF fuel may have led to a reduction in tin emissions.

The results of the titanium analyses showed blank train levels in excess of 30% of the sample results, with the 2019 LCF blank level being similar to the geometric of both the 2019 Baseline and 2020 LCF series. Titanium dioxide would be expected to be present in the raw meal, and differences may be related to the feed. The ReMAP assessment determined that the 2019 LCF results were outside the expected range of the other tests. The other tests overlap even though the means test comparisons produced significant statistics. A positive correlation was found between titanium and TSP and the TSP means were different between the 2019 LCF and combined Baseline tests, but the titanium means for this comparison were not significant. The data suggest that it is unlikely that the decrease in titanium emissions is associated with changes in fuel.

If differences cannot be explained by sampling variability, there are likely other factors influencing the emissions. While the specific cause of these differences cannot be identified from these data, it must be recognized that the raw materials used in the process are mined from deposits that would be expected to have naturally variable concentrations of metals. Studies at another Canadian facility have assessed the contribution of metals from both the fuel and raw materials processed in the kiln. With approximately 12 tonnes of raw feed per tonne of 50/50 coal/petcoke fuel, the study found that the raw feed contained much more barium, cadmium, chromium, lead, and thallium than the fuel contributed. Copper, vanadium and nickel concentrations in the fuel and the feed were similar. The fuel contributed more mercury and zinc than the raw feed, as the ratio of g/hr of these elements from the fuel and the raw material were less than the mass of fuel to the mass of raw feed. Molybdenum was not quantified in the fuel study.

Most minerals in nature are found in varying concentrations. Given the sedimentary nature of raw feed materials it is probable that the concentration of trace metals will vary from location to location within a deposit. Since the 2019 testing was separated by several months, the raw material being mined would be expected to be in a different location in the deposit, and thus the raw materials could have had different concentrations of the trace elements.

Comparing the metals emissions at Brookfield with those reported in the BAT requires considering 3 groups of metals: Mercury; the sum of Cadmium and Thallium; and the sum of Arsenic, Antimony, Lead, Chromium, Cobalt, Copper, Manganese, Nickel and Vanadium. Mercury data from this study is 4 ug/m³ at the low end of the BAT 0-30 ug/m³ range. Summing the average for cadmium and thallium the values from Brookfield are 27 ug/m³ again at the low end of the 0-680 ug/m³ range reported in the BAT. The final comparison is 70 ug/m³ at Brookfield versus 0-4,000 ug/m³ in the BAT. Overall, the metals emissions are at the low end of those reported from other facilities.

The independent samples t-test results from the comparison of means for the organic species targeted in the testing programs produced a limited number of significant statistics. As discussed for the individual compounds, many of the organics released in low concentrations from cement kilns are related to organics in the raw meal. These compounds are not exposed to the intense high temperatures and long residence times in the flame which should result in the destruction of most organic species.

Method variability data such as the ReMAP formulations are only available for the combined PCDD/F results as there is insufficient dual train testing data to assess method variability for the other species. However, the evaluation identified mixed results for PAHs, and the emissions of these compounds can be assumed to not be the result of fuel differences.

Without the ability to assess the precision of the VOST and Bag sampled organic tests based upon simultaneous sampling it is not possible to attribute the variability to method precision. These compounds produced mixed results similar to the PAH determinations. Some compounds are higher for the LCF test than the Baseline tests, but others are lower. This limits the ability to develop definitive statements about the effect of fuels on this group of compounds. Not as well documented is the presence of organic materials in the sedimentary materials that are fed to the kiln. Given the counter-flow nature of the process organics in the raw feed the BAT notes that these would be expected to volatilize as the feed is heated and can give rise to volatile organic constituents in the stack gas.

Examining the PCDD/F data using the ReMAP approach identified that the 2017 Baseline tests did not overlap with the other series indicating that the significant statistics might be meaningful. With the limited data from the 2017 tests and the high concentration on the first test, that conclusion should be viewed cautiously. The ReMAP calculation suggests that means differences from the 2019 and 2020 test series comparisons could be the result of method variability. It should be noted that all PCDD/F results are well below regulatory levels in Canada, and indeed the 2019 and 2020 results were below the Level of Quantitation used to define virtual elimination of these contaminants.

As discussed in the report, metals emitted from the stack are associated with fine particulate matter that escapes the ESPs. It is known that some organic species will bind to particulate matter, and the more available surface area there is, the more likely this is to happen. To determine whether variations in the particulate matter emission, TSP discussed earlier, might have influenced the emissions of other species a linear correlation was completed between the TSP and the other species. Only 4 metals were found to have significant positive correlations with TSP: calcium, lithium, strontium, and titanium. Both the organic species identified as having correlations with TSP emissions were negatively correlated, the concentration decreased

as the dust emissions increased. The identification of some species being correlated to particulate matter emissions is important since changes in the electrostatic precipitator performance might be expected to result in changes in the concentrations of these species.

What conclusions can be taken from these data? Recognizing that there are a limited number of cases in many of the comparisons, one might suggest that the results are inconclusive, but do indicate trends. On a subjective basis, the LCF runs produced the lowest PCDD/F TEQ values recorded in the 4 series, and the 2017 Baseline the highest values. As noted in the text, many of the emissions, regardless of whether the differences were significant or not, were at low concentrations.

INTRODUCTION

A.J. Chandler & Associates Ltd. was contracted to review the Stack Testing data from the Lafarge Brookfield facility. The scope of the project included comparisons of the Baseline emissions testing data from 2017 and 2019 with the data collected during special low carbon fuels [LCF] tests in 2019 and 2020. The Baseline testing was conducted when the kiln was fuelled with the normal fossil fuels used by the facility. The LCF tests in 2019 and 2020 involved the substitution of a portion of the normal fuels with a mixture of low carbon fuels including shingles and tires. The purpose of the measuring emissions during the use of low carbon fuels was to ascertain if there were significant changes in emissions arising from the use of low carbon fuels.

Testing was conducted according to pre-test plans approved by the staff of Nova Scotia Environment. The list of target species reflects those referenced in the facility's existing Approval document. Table 1 provides the full name of the species listed along with the units used for data presentation. The results for 220 species are shown in Table 2 and these were used for the analyses in this memorandum. Blanks in the table exist because either the species were not evaluated in the laboratory for a specific series, or the tests was not conducted for those species in a series.

Comparisons were conducted to assess if there were statistically significant differences between the mean reported emission values for each of the species for each test series. That is, the 2017 Baseline test data was compared to the 2019 Baseline, 2019 LCF, and 2020 LCF results. In turn, the 2019 Baseline was compared to each of the LCF series; the LCF series were compared; and each of the LCF series were compared to the combined Baseline data. Not all the species were reported for all four test series.

The comparison of Baseline series allows one to assess if differences in the composition of the raw materials introduced into the kiln or processing conditions may have caused changes over the intervening years. In reviewing the results of the statistical tests the practical significance of identified differences is discussed with respect to raw materials changes or operating changes.

TEST PROGRAM OUTLINE

Emissions testing at large industrial facilities is typically required as part of the operating permits issued by provincial regulatory agencies. In the case of the Brookfield facility, Nova Scotia Environment issued an approval for the use of low carbon fuels in July 2017. That approval required that the company submit a pre-test plan covering air emissions testing at the facility. The pre-test plan was approved for each of the testing series. Between series there were discussions with the agency and changes were made to the pre-test plans as dictated by agreement with the agency. Testing was to be conducted as outlined in the specific pre-test plan.

Overall, the results of the testing were satisfactory, but there were some limitations in the data collected for various series. In 2017, an impinger broke during collection of the SVOC sample for the 2nd test and the results were discarded; this results in only 2 valid results for PAHs, CBs, CPs PCBs, and PCDD/Fs for that series. At the laboratory the analyses did not provided mass collected results for aluminum and calcium. The list of PAHs analysed by the laboratory was not as extensive as that achieved in some of the later testing.

In 2019, it was agreed, based upon the 2017 results, that chlorophenols would not be analysed. The 2017 results found all compounds to be below the detection limit. The 2019 Baseline tests were judged acceptable by the agency.

For the 2019 LCF tests the agency identified that one of the targeted quality assurance measures for the SVOC, Halide, and metals tests was not met. The isokinetic ratio compares the velocity at which the sample is extracted through the sampling nozzle to the stack velocity at the sampling point. The velocity in the nozzle must be calculated from the volume of sample measured at each point after that volume has been corrected for gas temperature and pressure in the meter and the stack and the moisture content of the gas in the stack. This criterium is aimed at avoiding selective sampling of particular size particles due to inertial effects. *“If the sample velocity is too slow, sampling is said to be under-isokinetic. The small particles follow the fluid streamlines, which are bent away from the nozzle. The larger particles tend to follow straight lines due to their inertia. This makes them overrepresented in the sample, and the total particle load per gas volume will be higher, than that of the main gas stream.”*¹ The opposite effect occurs if the sample velocity is too high because the large particles have sufficient inertia to overcome the influence of the sampling. The potential influence of this effect was examined in the early 1950s and reported in a paper². The authors found that there was a mixed effect, errors were both \pm when large particles (400-500 μm) were introduced into the system at stack velocities from 1,000 – 3,000 fpm and nozzle velocities both greater and lesser than the stack velocity. For 80–100 μm dust sizes the error was 1.25 to 1.45 times the true weight when the nozzle velocity was 66% of the stack velocity, regardless of the velocity in the stack. For 5-25 μm dust the error increased to approximately 1.5 times for nozzle velocity 66% of the stack velocities; however, at lower isokinetic ratios, the effect on these particles increased at higher stack velocities. The results, regardless of particle size, showed that the actual mass collected was lower than the true mass if the nozzle velocities were higher than the duct velocity.

In the case of the 2019 LCF testing at Brookfield, the isokinetic ratio determined after testing was completed, was 5-10% lower than the minimum criteria specified in the methods. The testing company reported that this occurred due to an incorrect moisture being used for the set-up calculations. While this is likely to have resulted in an over-reporting of emissions, it was concluded that this testing would be repeated. For this reason no comparisons were made for SVOCs from the 2019 LCF testing and T3MP was removed for calculations involving TSP and metals. The 2020 LCF testing was used for these species. The 2020 LCF testing did not include VOCs or the stack gas monitoring completed in the earlier series.

¹ Ontario Source Testing Code [DRAFT \(dr6j45jk9xcmk.cloudfront.net\)](https://dr6j45jk9xcmk.cloudfront.net)

² Hemeon, W.C.L. and G.F. Haines Jr., 1954. [The Magnitude of Errors in Stack Dust Sampling \(tandfonline.com\)](https://tandfonline.com)

REVIEWING AND PREPARING THE DATA FOR STATISTICAL ANALYSIS

The data, as published in the stack testing reports, was reviewed for completeness and accuracy before being used to determine if there were differences between the test series. The stack sampling team extracts samples from the stack using established procedures. The samples collected are sent to a laboratory for analyses, and the results of the laboratory analyses are used by the stack testing team to calculate emissions from the facility for the specific test. When reviewing stack testing reports one might find transcription and typographical errors that should be corrected before using the data for statistical tests. Given the volume of data assembled, it has been the author's practice to use the laboratory data and the sample volumes calculated by the stack sampling team to repeat their calculation as a cross-check of potential errors.

There are issues that must be considered when creating a database to undertake statistical comparisons of test data. These include:

- the treatment of laboratory data that is reported to be below the detection limit [BDL];
- accounting for matrix interferences occurring during the analytical procedures;
- addressing the potential for contamination of samples caused by field procedures or reagent impurities; and,
- determining the amount of PCDD/F present in the samples when there are BDL values.

The effect of these situations on the data is presented in Appendix A, and the following paragraphs summarize how they were addressed for this study.

Below Detection Limit, [BDL], results indicate that the laboratory was not able to quantify the amount of a species in the sample collected. Laboratories typically report BDL values and stack testing reports substitute a value as directed by regulatory agencies. For this study, BDL values are identified in Table 2 with -ve signs before the laboratory reported values, for all species except the 2019 and 2020 metals tests. Since the laboratory uses 3 different portions of the samples to determine the mass of most metals and each could be BDL this report follows the US EPA recommendation of effectively substituting the reported DL in the summation.

Matrix interferences occurring during analyses can result in the laboratory reporting an elevated amount of the species to be present in the sample, and it can also raise the DL of the sample. By maintaining the laboratory's reported DL in the database, these situations are recognized and can be addressed if there are significant statistics found in the analyses.

Historically, the potential for contaminants to enter a particulate matter field sample has been addressed by analysing a "blank train sample" and compensating for any material found in the sample by deducting that amount from the test samples. This is not the procedure used for the metals sampling procedure; "field blanks" of various reagents and the filter are employed to correct for this. For this study, in the absence of field blanks for the metals tests, there was no correction for contaminants. Note: The SVOC and VOC sampling results are not corrected following the recommendations of Environment Canada.

PCDD/PCDF data are presented in the mass concentration units pg toxic equivalency (TEQ)/m³. PCDD/PCDF consists of 75 PCDD congeners (related compounds) and 135 PCDF congeners, each with varying levels of toxicity. The toxic equivalency is a number that represents the concentration of dioxins/furans in terms of the most toxic congener 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD). The initial concentration of each congener, in units of pg/m³, was multiplied by its respective toxic equivalence factor (TEF) as defined by WHO in 2005 resulting in units of pg TEQ_{WHO2005}/Rm³. As discussed in Appendix A, nondetectable levels of congeners can be found in laboratory results.

The stack sampling teams states, in their report, that if the analytical results for a congener was less than the detection limit, they simply substituted zero for that congener in the calculation of the pg TEQ_{WHO2005}/Rm³. Helsel³ (Helsel, 2010) suggests that the substitution approach creates a situation where the less precise data can have a large effect on the result particularly if the EDL is high. This can lead to erroneous results when hypothesis testing is performed. He cites the work of several authors showing the inadequacy of the substitution process and recommends the use of the Kaplan-Meier (KM) procedure that is frequently used in survival analysis for computing the mean of right-hand censored data. Essentially the procedure generates the mean of the congener values times their respective TEFs to provide a reliable method of predicting the mean TEQ value for the test and upper confidence limit of the mean. Helsel provides a spreadsheet⁴ that was used for this study. The resulting mean is based upon parametric procedures that do not require transformations or assumptions about the specific distributional shape of the data.

After accounting for these factors, the laboratory results are treated in a consistent manner to determine emission concentrations, the parameters examined in this study. The sample volume and stack oxygen concentration were used to determine emission concentrations for each contaminant in the form mass/Rm³ @ 11% O₂. These data are summarized in Table 2 appended to this memo. When the diluent levels, oxygen concentrations, were not available the data are expressed as mass/m³ whereas with the diluent correction the units are mass/m³ @ 11% O₂. As noted the negative sign on values in Table 2 designates the BDL values. Blank spaces indicate that the parameter data is not available for that particular series.

The resulting database contains test results for 220 species of interest. A testing series typically involves a total of 3 sampling tests during each series so a total of 12 results for each species would represent full recovery. There were species listed as possible targets for analyses but not identified in specific laboratory reports and these have been dropped from Table 1 and Table 2. There were 2 species, 1,2 Dichlorobenzene and Methyl Chloride [Chloromethane] that were sampled by different methods and produced different results. The higher of the two results for Methyl Chloride was retained for these analyses. Dropped were both 1,2-Dichlorobenzene results as they were less than detected as were the results for the other isomers 1,3-Dichlorobenzene and 1,4-Dichlorobenzene. While listed in the tables, chlorophenols were only targeted in the 2017 Baseline tests and all but two results for these 16 species were below the detection limit. These species were dropped from these analyses. Also dropped were: chlorodibromomethane; 1,1,2,2-Tetrachloroethane;

³ Helsel, Dennis R. 2010. "Summing Nondetects: Incorporating Low-Level Contaminants in Risk Assessment." *Integrated Environmental Assessment and Management* (6): 361-366.

⁴ Helsel, Dennis R. n.d. KM Stats v1.5. Accessed March 3, 2014. http://www.practicalstats.com/nada/downloads_files/KMStats15.xls.

and 1,2,4-Trichlorobenzene that all had values below the detection limit. The result of excluding the species mentioned above is that the total list is reduced to 196 individual species.

Statistical tests apply to data that are normally distributed. Typically, environmental data and stack sampling results are not normally distributed, and to normalize these data to allow statistical testing, the data can be transformed to the logarithmic plane. The emission concentration database discussed above was read into SPSS for Windows, Version 19.0.0 to complete the statistical analysis for this study. The conversion to the natural logarithm [Ln] of the concentration was completed in SPSS.

When the log transform is performed in SPSS the BDL values designated by the -ve sign are set to missing since there is no meaning to the log of a negative number. Excluding such data reduces the number of test values available for comparisons. Table 3 shows the resulting number of values available for comparison by test series and comparison.

Table 3 Summary of Test Results by Series

Number Of Cases	Comparison Groups											
	Base17	Base19	Base17	LCF19	Base17	LCF20	Base19	LCF19	Base19	LCF20	LCF19	LCF20
3	44	107	44	19	43	79	60	20	107	80	9	37
2	46	14	2	47	46	7	6	46	14	7	34	1
1	16	11	9	8	16	7	5	8	11	7	0	1
0	92	66	53	34	92	104	37	34	66	104	0	4
Total	198	198	108	108	197	197	108	108	198	198	43	43

The differences between the total number of cases compared is due to the elimination of some tests from comparison. Since the T3MP test from the 2019 LCF series was unacceptable it was removed from consideration as were all three SVOC tests from that series. The absence of gas monitoring and the VOCs from the 2020 LCF test series limited the number of comparisons that could be made with that series. The most severe restrictions occurred for the comparison of the LCF series because the gases, VOCs and SVOCs could not be compared, and the metals were only available for 2 runs in the LCF19 series.

Statistical Comparison Procedures

Statistical tests were used to determine if a change in raw materials, or process conditions resulted in a change in emissions. Typically stack test data varies over a limited range for any test series. One of the reasons for conducting 3 tests is to identify the variation inherent in the emissions. The result of the 3 tests can be averaged for regulatory purposes, but it is inappropriate to simply consider the differences between the mean values to determine whether there have been changes. One must account for the inherent variation present in the stack emissions before concluding that the data are the same or different.

Determining the significance of the apparent differences was the objective of this study. This was accomplished using the Independent Samples t-Test in SPSS. This procedure compares means for the two different conditions taking into consideration the variation between the individual test results in the groups. The test establishes whether the means are similar, statisticians call this the null hypothesis, and determines the significance of results that suggest that they are not the same. It is not possible to use the t-Test to define the source of the difference, merely to identify that there is a difference.

One statistic generated by the method is a measure of the significance of the result. This indicates the probability associated with the determination that the means are not the same. It tells the researcher how often the test might be wrong when it indicates a difference. This significance is designated as α or [Sig.] in most results. This decimal value, which can range from 0 to 1. If a value of 0.05 is selected there is a possibility that 1 in 20 comparisons might produce the wrong conclusion, that is even though the test indicates there is a difference that might not be the case. Most researchers use significance levels of 0.1 (one in ten) or 0.05 (one in twenty) as reasonable criteria to determine the chance that the results may be incorrect. If the researcher senses that the consequences of an incorrect conclusion are more dire, they might want to select a ninety nine out of a hundred (0.01) significance level. In the comparison of means we assume that the means are the same, and the significance level suggests that they are not.

For statistical tests, there are minimum requirements for the data:

- The two groups must contain independent observations.
- The data should be a random sample from the population.
- The data should fit a normal distribution.
- The variances in the data of the different groups should be approximately equal, to provide the highest confidence that the tests results are trustworthy.

Since testing was done under different operating conditions, either in different years or with different fuels, the results are independent. They are also random because there was no specific schedule to the testing. Typically stack data will have a considerable amount of data at lower concentrations and limited amounts of data at higher concentrations. To overcome this, data for the study was transformed as discussed earlier. As discussed below it is possible to calculate an approximate statistic that is not based upon assuming equal population variance, and this was done in this study.

As with any statistical test, the more data points that can be compared the more certainty can be derived from the result. Since this study is comparing the triplicate results of Base or LCF stack tests conducted under different conditions, the maximum number of cases for any specific testing is 3 samples. This is fewer than the minimum of 6 sample preferred by most statisticians when they use this test. While this increases the uncertainty, the statistical approach does provide an indication that observed differences should be considered. Having identified such results, the tests can be examined to determine if the findings are related to changed conditions. Ideally if there is no statistical difference between conditions, the data could be combined to increase the certainty of the results.

The SPSS procedure for these calculations includes Levene's test for equality of variances and both pooled-variances and separate-variances t-tests for equality of means are determined. For the equal-variance t test, the observations should be independent, random samples from normal distributions with the same population variance. For the unequal-variance t-test, the observations should be independent, random samples from normal distributions. The program calculates the Levine Statistic for the contaminant and provides t-test results for the Equality of the Means. For this study, the significance of the Levine significance statistic was selected to be 0.10. If the statistic was greater than this the two sample groups were assumed to have equal variances and the t-test for equal variances can be applied. When the Levine statistic was less than 0.10, the t-test for unequal variances was used.

For the Independent Samples t-Test a 95% significance level was employed. A 2 tailed significance level that is less than 0.05 was thus considered significant and the difference in the mean values for the tests was assumed to not be due to chance alone. SPSS provides the output of the independent Samples t-Test in the form of two tables that are provided at the end of this report.

The first table contains the means test statistics for both the condition where the variances are assumed to be equal and where equal variance was not assumed. Two columns provide the Levene's Test for Equality data: the F statistic and the significance of that statistic. If the significance is greater than 0.1 the equal variance condition is satisfied. The t-test for Equality of Means generates 7 columns of data: t-statistic; 2 tailed significance of the t-statistic; Mean Difference between the values for the groups; Standard Error of the Difference; and the upper and lower 95% Confidence Interval of the Difference. The latter provides an estimate of the boundaries between which the true mean difference lies within 95% of all possible random samples of test results. If the Significance is greater than 0.05 the test suggests that one can accept the assumption that the means of the two groups for that specie are similar. Since the tests were completed using the log-transform of the test results, they are difficult to interpret directly. Rather, the results should be considered an indication that there is a reason to further review the data.

The second table produced by the analyses contains the Group Statistics for the tests under consideration. The columns in the table are: Component or Species being considered, and then there are 4 groups of two columns, one for each group of data being considered. The column groups include: the number of samples; the mean of the log-transformed values; the standard deviation of those values; and the standard error of the log-transformed mean. The number of samples for each target species and each test series provides an indication of how many results can be compared for the given species. For convenience, the geometric mean of the test data for each series has been included in this table. These values are the exponential values of the log-

transformed mean values in the table. These allow the reader to quickly see which of the indicated test series resulted in the higher emission levels.

Each comparison creates two rows in the t-statistic output and one row in the Group statistic output. To limit the number of pages of tables, only the species which produced t-statistics that were significant are included in this report. The full results are available as 8 separate EXCEL files.

As noted earlier, variations in contaminant values are typical in most stack data. Any triplicate would be expected to have some variability, but changes in sampling procedures, analytical procedures or process can result in year over year variation too.

The sampling location was different for the 2017 data compared to the 2019 data. Samples were taken from the stack in 2017, whereas the 2019 sampling was done in the breeching where the gases are introduced to the stack. It is not known if this induces a difference in the values determined.

While not shown in Table 2 sampling times were similar between tests, and as such sample volumes were similar. Two exceptions were noted: the 2019 LCF tests have lower sample volumes for the SVOC testing; and, the 2020 LCF SVOC testing duration was increased from 144 minutes to 192 minutes. This would result in larger sample volumes which would have the potential to reduce the number of BDL values. While it is the author’s preference that PCDD/F and Metals testing be completed over a period of 4 hours, the sampling at Brookfield was completed in 2.4 or 3.2 hours. Shorter sampling times result in smaller sample gas volumes and less averaging of the variations in emissions as well as potentially raising the number of non-detects in the laboratory analytical results.

The full output from the statistical analysis produces data for each of the 198 species listed for each test series, however, as can be appreciated from Table 3 the blanks and negative values limit the number of species that can be compared. The number of comparisons completed for each combination are listed in Table 4.

Table 4 Summary of Number of Comparisons completed by Combination

Test Series Comparisons		Comparisons Available
Test Series A	Test Series B	
Baseline 17	Baseline 19	101
Baseline 17	LCF 19	56
Baseline 17	LCF 20	70
Baseline 19	LCF 19	69
Baseline 19	LCF 20	85
LCF 19	LCF 20	39
LCF 19	Baseline 17 and Baseline 19	70
LCF 20	Baseline 17 and Baseline 19	90

Table 5 summarizes the number of significant comparisons identified by the independent means t-test, at the 95% level. Both the number of significant comparisons and the percentage of the total comparisons these

represent are shown in the table. To further define the species that accounted for statistically significant means from the testing, Table 5 lists the species divided into 6 broad categories:

- Gases – CO; NO_x; SO₂; THC; and NH₄ are created during combustion;
- Particulate Matter [TSP] – dust released from the process; not listed in the size fractionated particulate matter results (PM₁₀ and PM_{2.5}) which were considered.
- Metals – with the exception of mercury, the metals are released as part of the dust released;
- SVOC – semi-volatile organics including CPs, CBs, PCBs, and PAHs (polyaromatic hydrocarbons) but excluding the PCDD/Fs that are listed separately;
- VOC – volatile organic compounds are any organic compounds having an initial boiling point less than or equal to 250° C measured at a standard atmospheric pressure of 101.3 kPa. VOCs were not included in the 2020 test series accounting for the blanks in the table.
- PCDD/F – dioxins and furans including the 17 congeners include in calculating the TEQ; the 8 homologues that represent the sum of compounds with the same chlorination level; and the KM TEQ_{WHO 2005} value that is calculated from the congener values.

There were no significant differences identified for the halides: HF, HCl, and Cl₂.

Table 5 Summary of Significant Comparisons

Test Series Comparisons		Significant Comparisons	Species Compared and Number Considered					
Test Series A	Test Series B		Gases	TSP	Metals	SVOC	VOC	PCDD/F
			5	1	32	54	75	26
Baseline 17	Baseline 19	16 (16%)	3	0	7	1	3	2
Baseline 17	LCF 19	13 (23%)	3	0	5	0	5	0
Baseline 17	LCF 20	12 (17%)	0	0	6	1	0	4
Baseline 19	LCF 19	20 (20%)	3	0	14	0	3	0
Baseline 19	LCF 20	29 (34%)	0	0	16	11	0	2
LCF 19	LCF 20	11 (28%)	0	0	11	0	0	0
LCF 19	Baseline 17 and Baseline 19	20 (27%)	2	1	10	0	7	0
LCF 20	Baseline 17 and Baseline 19	26 (29%)	0	0	13	8	0	5

The discussion of the statistically significant mean differences identified during this study will address each category separately. Where there might be relationships between species and their behaviour extra sections are included.

It is important to note that the independent means test only identifies differences, it does not provide any information on the reasons for the differences. There are several broad explanations for differences in the means:

- For some elements and compounds changes in the raw materials introduced into the process can give rise to differences in emissions.
- The concentration of elements in the exhaust can be influenced by changes in the fuel used in the process.
- Process changes that influence the performance of the electrostatic precipitator [ESP] can also influence emissions.
- The sampling methods employed to collect and analyse the samples will produce some variation in the results, even if the actual stack concentrations do not change.

Assigning a cause to the differences is not possible given the limited data collected to date. A more detailed experimental design that fixes certain parameters while allowing others to vary could provide insight, but this would be difficult in a process that uses natural materials as the feed stream unless all the feeds to the system were also sampled and analysed. Studies documented in the literature can provide a list of the factors affecting ESP performance, but these were beyond the scope of this work. There is a method that can be used to address the last effect for at least some of the targeted species, and that will be applied as the second step in this evaluation.

To address the variability in the concentration of measured species, it is possible to do simultaneous sampling with a second set of sampling equipment and compare the results. This approach was used to validate stack sampling methods when they were developed. Simultaneously collected data also provides an opportunity to assess the potential variability in the method at different concentrations of the species in the stack gas stream.

For assessing the precision of the method, calculations of the relative standard deviation [RSD] of the method are used. The RSD is calculated as the standard deviation of the results divided by the mean of the results. Values reported by CARB⁵ notes that RSD values for Cd, Cr, Cu and Pb are in the range of 11.2 – 11.6%, whereas the RSD for As is 13.5% and Ba is 20.6%. These were based upon tests at a sewage sludge incinerator.

Another study, ReMAP⁶, looked at the variability of data at different average concentration levels and determined the accuracy and precision of the reported data at different concentrations for a range of different test methods. In contrast to the CARB study, the ReMAP analysis showed the RSD from simultaneously collected Cd data was in excess of 75% at a concentration of 1.4 ug/dscm, dropping to 38.6% at 5 ug/dscm, 18.7% at 20 ug/dscm and 9.1% at 80 ug/dscm. To date the ReMAP procedure has only considered variability for Methods 5 (Particulate Matter); Method 23 (PCDD/F); Method 26 (HCl) and Method 29 (Metals). See Appendix B for a discussion of ReMAP procedures and a summary of the relationships identified between the concentrations measured and the standard deviation identified from the regression analyses.

These data are important when considering results that produce significant statistics for the t-test comparison of means. If the anticipated variability in the results covers the range of the values being compared, it could suggest that there is little reason to suspect an environmentally meaningful difference between the values regardless of the statistical results.

⁵ California Air Resources Board, 1997. Method 436 Determination of Multiple Metals Emissions from Stationary Sources.

⁶ W. S. Lanier and C. D. Hendrix, "Reference Method Accuracy and Precision (ReMAP): Phase 1 Precision of Manual Stack Emission Measurements," ASME International, 2001.

Discussion of Statistical Results

The main emissions from the production of cement are to the air from the kiln system. These derive from the physico-chemical reactions involving the raw materials and the combustion of fuels. The main constituents of the exit gases from a cement kiln are nitrogen from the combustion air; CO₂ from calcination of CaCO₃ and combustion of fuel; water vapour from the combustion process and from the raw materials; and excess oxygen.⁷ Minor constituents in the emissions are carbon monoxide, oxides of nitrogen, sulphur dioxide, ammonia, chlorine and hydrogen chloride, and total hydrocarbons (combustion gases); metals; and, organic contaminants including volatile organic compounds, semi-volatile compounds, and PCDD/F. The discussion that follows includes information about the formation and distribution of the species in the process as identified in the referenced documents. All values for species included in this section of the report are the geometric mean values for the test series shown in the Group tables at the end of the report.

Combustion Gases

With the exception of NH₄, the combustion gases were sampled in real time with the 1 minute readings from the instruments. By averaging these values over the sampling period, 3 test averages were available for each test series. NH₄ was determined from a grab sample collected over a specified time period. The results from each of 3 tests were reported for each series. Real time readings provide an indication of fluctuations in the concentration of the specie being monitored; grab samples do not provide an indication of how the concentrations might have varied over the sampling period.

Carbon Monoxide [CO]

The European Commission BAT document referenced above suggests that emissions of CO and organically bound carbon during the clinker burning process are caused normally by the small quantities of organic constituents input via the natural raw materials (remnants of organisms and plants incorporated in the rock in the course of geological history). These are converted during kiln feed preheating and become oxidised to form CO and CO₂. In this process, small portions of organic trace gases, such as total organic carbon, are formed as well. In the case of the clinker burning process, the content of CO and organic trace gases in the clean gas do not allow any conclusions on combustion conditions induced by fuel changes.

The report goes on to point out that additional CO emissions may also result from poor combustion and improper burning conditions in the secondary firing. Typically, the report suggests that poor combustion leading to increased CO emissions rate coincides with a decrease in the NO_x emissions. Such reducing conditions may also have a positive effect on SO_x emissions. This suggests that responses in combustion gas emissions can be linked.

⁷ European Commission, 2013. Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide. A Reference Report by the Joint Research Centre of the European Commission. Report #JRC 83006 published by the EU #EUR 26129 EN Available at: <https://ec.europa.eu/jrc/en/publication/reference-reports/best-available-techniques-bat-reference-document-production-cement-lime-and-magnesium-oxide>

CO differences were identified for the comparison of the baseline tests, 2017 vs 2019 and the 2017 tests Baseline versus 2019 LCF as well as 2019 Baseline vs 2019 LCF. The geometric mean values for the tests are shown below:

Geometric Mean	2017 Baseline	2019 Baseline	2019 LCF	Combined Baseline
Carbon Monoxide [mg/Rm ³ @ 11% O ₂]	217	304	255	257

The common value for the comparisons that were significant is the 2019 Baseline CO level. Even with the variability, the Brookfield results are at the low end of the data that the BAT document reports from CO from European cement kilns.

Lafarge undertook total organic carbon [TOC] testing on the kiln feed streams for the two 2019 test series. The company has noted a relationship between total graphitic carbon and CO production in the past. The testing of two feed samples from the 2019 Baseline test period showed 0.34% and 0.24% graphitic carbon versus the two samples from the 2019 low carbon fuels test period at 0.30% and 0.18% graphitic carbon. The graphitic carbon changes in the feed might explain the CO differences. As noted in the BAT document, elevated CO can also be related to poorer combustion conditions. Typically, CO production increases if there is limited oxygen available to complete the conversion of CO to CO₂. The 2019 Baseline testing showed an average O₂ level during CO testing of 4.99% versus the 5.2% during the low carbon fuels testing.

The data indicates that low carbon fuels did not produce a significant statistic when compared to the combined Baseline data suggesting that there the range of the Baseline values reflects typical variability and the LCF run was in the middle of that range. This suggests that low carbon fuels had no affect on CO emissions.

Oxides of Nitrogen [NO_x]

NO_x can be formed through any of four processes in a cement kiln:

1. Thermal
2. Fuel
3. Feed
4. Prompt

Thermal NO_x is produced from the reaction of atmospheric nitrogen and oxygen at high temperatures. Another important parameter in the production of thermal NO_x is the gas-phase residence time⁸, the longer the residence time and the greater the temperature, the higher the thermal NO_x emissions will be. Typically, Lafarge cement kilns have approximately a 10 second residence time in the zone with greater than 1000 C temperature.

Fuel NO_x is produced from the oxidation of nitrogen content in the fuel. Feed NO_x, like fuel NO_x, is produced from the oxidation of nitrogen content in the raw feed. The USEPA suggest that it is unlikely that these factors will contributor significantly to NO_x emissions at a cement facility.

⁸ US EPA, "Alternative Control Techniques Document- NO_x Emissions from New Cement Kilns," US EPA Office of Air Quality Planning and Standards, 2007.

Finally, prompt NO_x is from the reaction of atmospheric nitrogen and hydrocarbon radicals. The contribution of prompt NO_x is relatively low compared to the other sources in a cement kiln.

According to the USEPA it is difficult to determine the quantity of fuel and thermal NO_x; however, thermal NO_x is thought to be the main contributor to NO_x emissions from cement kilns. This makes sense since the process is high temperature with long residence times.

It is therefore possible that changes in in the facility's flame temperature could lead to the varying NO_x emissions and CO emissions. The BAT document suggests that there might be an inverse relationship between CO and NO_x which could also arise from differences in the oxygen levels. Comparing the CO and NO_x data suggests that this relationship holds for the Brookfield test data. Further causative analysis would be required to determine if there was a change in flame temperature was due to fuel changes between the various series of tests. Factors such as an increase in the primary air injection flow rate could influence such changes.

The BAT document notes that NO_x emissions vary depending on which kiln process is used. Besides temperature and oxygen content (air excess factor), NO_x formation can be influenced by flame shape and temperature, combustion chamber geometry, the reactivity and nitrogen content of the fuel, the presence of moisture, the available reaction time and burner design. On a yearly average, the European cement kilns emit about 785 mg NO_x/Nm³ (expressed as NO₂) with a minimum of 145 mg/Nm³ and a maximum of 2040 mg/Nm³. The data included in this study is at the low end of that range.

Geometric Mean	2017 Baseline	2019 Baseline	2019 LCF	Combined Baseline
Nitrogen Oxides [mg/Rm ³ @ 11% O ₂]	968	596	778	759

NO_x was identified as having a significant difference in the mean values for comparison of both the Baseline 2017 vs 2019 series and Baseline 2017 vs LCF 2019 and Baseline 2019 vs LCF 2019. The differences between the mean values for the combined Baseline tests and the 2019 LCF test were not significant. The variability within and between tests should be considered with respect to the potential generation of NO_x in the kiln. Given that the test of the combined Baseline data and the LCF results did not produce a significant statistic, it would appear that the effect of using LCF on NO_x is limited.

Sulphur Oxides [SO_x]

The BAT suggests that SO₂ emissions from cement plants depend on the total input of sulphur compounds and the content of the volatile sulphur in the raw materials. While fuels may influence the sulphur releases, they have less effect on emissions. The production and potential emissions of SO_x also depend on the sulphur circulation which occurs in the kiln system: SO₂ in the exhaust gases, CaSO₄ and other combined compounds in the clinker and the dust. Regardless, the greater part of the sulphur is incorporated into the clinker or the dust discharged from the process.

Depending on their respective deposits, the raw materials in the kiln feed may contain sulphur bound as sulphate or sulphide. Sulphates are stable compounds, only partly thermally decomposed at the high

temperatures prevailing in the sintering zone of rotary kiln systems. However, the decomposition can be increased by localised reducing conditions. Under most circumstances, the sulphate form is completely discharged with the clinker. Sulphides, by contrast, are oxidised in the preheater and partly emitted in the form of sulphur dioxides.

Sulphur introduced into the kiln system with the fuels is oxidised to SO₂ and will not lead to significant SO₂ emissions, due to the strong alkaline nature in the sintering zone, the calcination zone and in the lower stage of the preheater. This sulphur enters the calcining zone of the kiln system together with the minor concentrations of SO₂ resulting from partial sulphate decomposition in the sintering zone. In the calcining zone, SO₂ reacts with alkalis and alkali sulphates originating from the raw materials.

Elevated SO₂ emissions are to be expected when raw materials containing organic sulphur in a readily oxidizable form, e.g. as pyrite or marcasite. In contrast with the sulphatic raw material components, these readily oxidizable compounds may be converted to SO₂ as early as in the upper cyclone stages. Under these conditions, raw material related SO₂ emissions concentrations may be high.

Geometric Mean	2017 Baseline	2019 Baseline	2019 LCF	Combined Baseline
Sulphur Dioxide [mg/Rm ³ @ 11% O ₂]	658	616	391	637

The mean values of SO_x were identified as having a significant t-statistics for the comparison of the LCF test and to both Baseline tests as well as the combined Baseline category. 2019 low carbon fuels results were negatively skewed, the presence of low value separated from the other data. The Baseline tests were positively skewed with higher values and more variability. Overall, the average for the Baseline tests was higher than the LCF tests. Compared to European data in the BAT, all the SO₂ emissions are in the same range.

Total Hydrocarbons [THC]

The BAT addresses Total Organic Carbon emissions noting that while TOC emissions are typically associated with incomplete combustion, this is unlikely to be the case in a cement kiln with long residence times at high temperatures. These are the conditions that will result in minimal TOC emissions, i.e. >99.9999% destruction efficiencies. Emissions of volatile organic compounds can however occur from the primary steps of the process (the pre-heater and precalciner), when organic matter is present in the raw meal. These compounds are volatilized at temperatures in the range of 400 to 600 C typical of the temperatures in the early steps of the process. As noted in the CO discussion above, the test data identified that there were higher TOC levels in the 2017 Baseline feed versus the 2019 feed testing. This could explain the differences in the means for THC. The BAT document notes that most TOC emissions from 27 German kilns were in the <30 mg/m³ range, well above all test data from Brookfield.

Geometric Mean	2017 Baseline	2019 Baseline	2019 LCF	Combined Baseline
Total Hydrocarbons [mg/Rm ³]	12.6	7.8	6.6	9.9

Comparison of the mean values for THC identified that only the 2019 LCF comparison to the combined Baseline results produced a significant statistic. While there appears to be a difference between the Baseline values, the 2017 Baseline results had a very high variability and Levene's test was not satisfied and the resulting t-statistic for the comparison had a significance of 0.1 well above the 95% threshold used for this study.

The data indicates that the 2019 LCF testing results had lower THC emissions. Without comparing inputs from the raw meal and the fuels causality cannot not be assigned for this result.

Ammonium [NH₄]

Gartner and Wilk⁹ note that sedimentary materials, those used as raw materials in the cement manufacturing process, can contain measurable amounts of chemically bound nitrogen. Citing others, the authors state that these compounds would be converted to NO_x during combustion in air. However, small amounts of ammonium salts have been found in cement kiln dust and air emissions. At the time of writing, they said that the source of the ammonium had not been determined. Chemical kinetics suggests that there is a negligible chance that any ammonia would survive the high temperature, long residence times in the oxidizing environment of a cement kiln. Thus, the authors attribute the source of the ammonia to the incoming kiln feed. They postulate that since nitrogen in the kiln feeds will be in the form of complex organic molecules which have varying degrees of volatility there is the potential for them to be pyrolyzed to lower molecular weight species such as ammonia and thus be released to the atmosphere. Since the pre-heater and precalciner area of the process have lower temperatures, the volatilization and pyrolysis processes could give rise to ammonia releases from the feed stocks.

Tests of the Ammonium data produced a significant statistic for only the comparison of the Baseline tests. The variance for the 2020 LCF test was very large and this reduced the significance of the difference to the 2017 Baseline series.

Geometric Mean	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Ammonium [mg/Rm ³ @ 11% O ₂]	9.6	5.8	6.5	3.6	7.5

The averages for all the tests were less than 10 mg/m³ which is at the low end of the values reported in the BAT. The difference between the baseline runs likely reflects differences in the feed stock between 2017 and 2019, and the statistic indicate that there is no significant difference between the baseline and low carbon fuels emissions.

⁹ Gartner, E.M. and Ch. M. Wilk, 1987. The influence of raw materials on nitrogenous emissions from cement kilns. Available at <https://www.researchgate.net/publication/260426726> The influence of Raw Materials on Nitrogenous Emissions from Cement Kilns

Total Suspended Particulate Matter [TSP]

Particulate Matter, dust, is measured as part of the Method 29 train used to collect samples of the metals leaving the stack. The clinker burning process involves handling large quantities of dusty materials that can lead to emissions however the use of electrostatic precipitators to control dust emissions can achieve low emission levels. Electrostatic precipitators are sensitive to particle morphology and changes in the gas stream in which they are placed. Under steady state operating conditions, the operating parameters of ESPs can be adjusted to optimize control efficiency.

As discussed in the Test Program Outline earlier, one of the Method 29 test results from 2019 LCF was designated as questionable by NSDE due to the low isokinetic ratio. The effect of this limitation would be to increase the mass of particulate matter captured by the sampling system and thus the emission rate. The moisture levels in the 2019LCF were higher than those in any of the other testing, and changes in the moisture level in the stack have been documented to influence ESP performance.

The only significant difference identified for TSP was the 2019 LCF tests compared to the Combined Baseline test data. The LCF 2020 testing was not significantly different when compared to any of the other tests. The statistic for the comparison to the edited 2019 LCF test with the combined Baseline data had a significance of 0.045, close to the criteria. Clearly, the 2019 LCF runs were outside the range seen by the other tests.

Geometric Mean	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Dust [mg/Rm ³ @ 11% O ₂]	30	43	68	38	36

TSP was measured with the Method 29. This method was based upon US EPA Method 5 with changes to the impinger train to capture mercury and other metals. The method was validated by the US EPA and ReMAP utilized available data to develop statistics for the precision of the method. ReMAP, discussed in Appendix B and in the section that reviews the Metals data, developed an expression that defines the range of values that might be expected to result from measuring a specific concentration in the stack many times. Applying that approach to the 2019LCF data using the average of the test runs, 95 out of 100 future measurements would be expected to be between 19 and 138 mg/m³, a range that encompasses the averages of all the testing completed. This indicates that the precision of the method may account for the differences identified. The fact that there are no differences between the 2020 LCF results and the Baseline tests suggests that low carbon fuel operations had no affect on emissions of dust from the stack.

Particulate Matter less than 10 µm [PM₁₀] and [PM_{2.5}]

Comparing the PM₁₀ results for the various series, only the 2017 Baseline comparison to the 2020 LCF test showed a significant statistic. The geometric means were 18.1 and 28.7 respectively, with the other tests geometric means being 27.4 and 42.3 for the 2019 Baseline and 2019 LCF. The 2017 data would appear to be low but other comparisons were biased by high variability. Since the 2019 and 2020 tests did not produce significant statistics, low carbon fuels are unlikely to have influenced this result.

The PM_{2.5} comparisons did not identify any significant differences in the means.

Behaviour of Metals in Kiln

Producing clinker in the kiln involves exposing the raw materials to high temperatures. The BAT document referenced earlier states:

Many components that result from the combustion of the fuel or from the transformation of the raw material into clinker remain in the gas phase only until they are absorbed by, or condensed on, the raw material flowing countercurrently.

These materials thus are combined into the clinker produced by the process. The BAT document offers the following details:

Raw materials and fuels will always contain metals. Their concentrations vary widely from one location to another and the potential for emissions to the atmosphere is affected by very complex mechanisms. Furthermore, metal concentrations from wastes used as fuel varies with the waste origin. Metal compounds can be categorised into four classes, based on the volatilities of the metals and their salts:

- 1. Metals which are or have compounds that are refractory or non-volatile, such as Ba, Be, Cr, As, Ni, V, Al, Ti, Ca, Fe, Mn, Cu and Ag: these metals are completely absorbed by the clinker and discharged with it, and therefore do not circulate in the kiln system. In the exhaust gas, the only emissions are with the dust; they depend only on the input and the efficiency of dust segregation. Consequently, emissions are generally very low.*
- 2. Metals that are or have compounds that are semi-volatile: Sb, Cd, Pb, Se, Zn, K and Na: these metals condense as sulphates or chlorides at temperatures of between 700 and 900°C; and inner circulation occurs. In this way, the semi-volatile elements which are accumulated in the kiln's preheated system are precipitated again in the cyclone preheater remaining to a high extent but almost completely in the clinker.*
- 3. Thallium: metal that is or has a compound that is volatile: thallium compounds (e.g. TlCl) condense at between 450 and 550°C, in the case of heat exchanger kilns, in the upper area of the preheater, where they can accumulate (inner circulation).*
- 4. Mercury: metal that is or has a compound that is volatile: mercury and mercury compounds pass for the most part through the kiln and preheater; they are only partly adsorbed by the raw gas dust, depending on the temperature of the waste gas.*

An electrostatic precipitator [ESP] is used at the facility to control dust emissions from the stack. Most metals emitted from the stack are related to the fine particulate matter that escapes from the ESP.

Based upon the preceding there is a possibility that variations in the TSP emission rate could give rise to variability in the emissions of various elements and compounds that are associated with the fine particulate released from the stack. To test this hypothesis the correlation between TSP and emissions was examined.

Correlation between TSP Emissions and Emissions

Both metals and organic compounds can be associated with fine particulate emissions. In the cement kiln, most metals would be expected to be incorporated into the clinker formed in the process, but particulate matter escaping the system would be expected to have measurable metals concentrations. Many organic compounds, particularly SVOCs have an affinity for sorption¹⁰. Adsorbent media can include activated carbon, biochar, modified clay minerals. PAHs removal efficiency or adsorption/absorption capacity largely depends on several parameters such as particle size of the adsorbent, pH, temperature, solubility, salinity including the production process of adsorbents. Given these characteristics it is likely that some of the organic compounds identified in this study might bind with dust in the process and be released in much the same way as metals, with fine particulate matter.

To examine if changes in the TSP levels could explain the metal and organic compound emission differences, a determination of the correlation between TSP and emissions was undertaken. A linear correlation might be expected between the particulate emissions and emissions of particulate bound metals and organics. To investigate the relationship, SPSS was used to determine the bivariate Pearson Correlation between TSP and various species. Table 6 displays the results of the Pearson test for Ln transformed test data discussed in this report. Pearson Correlation values range from -1 to +1 with the negative values indicating an inverse relationship between particulate matter emissions and species concentrations and positive values indicating a direct relationship: as particulate matter levels increase the species emissions increase. The table shows only the significant correlations identified by the testing.

Considering all the data, the correlations with TSP were significant for: Ca, Li, Sr, and Ti. This suggests that tin emissions were lower when TSP emissions rose. The metals correlations indicate that increased emissions may have been partially explained by the increase in particulate emissions. Extending the Pearson correlation analyses to the organics: trichlorobiphenyl, and octachlorobiphenyl had significant correlations with particulate emissions. These correlations were negative, indicating that the compound concentration decreased with increasing TSP emissions.

Table 6 Pearson Correlation Statistics for Particulate Emissions and Species

Element/Compound	Pearson Correlation	Significance (2-Tailed)	Number of Cases
LnCa	0.743	0.035	8
LnLi	0.657	0.028	11
LnSr	0.771	0.005	11
LnTi	0.825	0.002	11
LnTRICBP	-0.729	0.040	8
LnOCBP	-0.848	0.033	6

¹⁰ Lamichhane S, Bal Krishna KC, Sarukkalige R. Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review. Chemosphere. 2016 Apr;148:336-53. doi: 10.1016/j.chemosphere.2016.01.036. Epub 2016 Jan 25. PMID: 26820781.

Analysis of Metals Emission Results

Metals are sampled using a grab sample technique, with portions of the sample being taken at different locations on various axes of the stack gas flow. US EPA Method 29 was used for metals sampling for the studies being considered in this report. The list of 32 metals targeted for analysis are shown in Table 1. The list includes the 17 species for which the method has been validated: Sb; As; Ba, Be; Cd; Cr; Co; Cu; Pb; Mn; Hg; Ni; P; Se; Ag; Tl; and Zn. Method 29 suggests that the other species quantified during analyses should produce valid results if the concentrations are at similar levels. In some cases, the validation process failed to measure some species and thus the performance could not be validated.

A total of seven of the metals validated for Method 29: Sb, As, Be, Cd, Cr, Pb, and Hg, were evaluated in the ReMAP study. As with the US EPA evaluation, the ReMAP report suggests that the variability in those results likely would be reflected in the other metals analysed in the same samples. Because of the paucity of duplicate data for other metals, confirmation of this interpretation could not be completed by the ReMAP study.

To assess if there were significant differences in the mean values for different test series, two different approaches were used. As with the gases and organic species each series was compared to the other series and the LCF series, both 2019 and 2020 were compared to the combined Baseline series. In addition, the comparisons were repeated after removing the suspect T3MP case from the LCF 2019. This resulted in 4 additional comparisons being completed. In the tables that follow the revised geometric mean for the 2019 LCF series are provided in parentheses. If an asterisk is provided after the parentheses, the revised mean moved closer to the other data and was found to not be significantly different from the other tests.

Table 5 identifies that out of the 32 metals quantified during the testing between a quarter and half of the results produced significant differences when the means of the tests were compared. The corollary to this finding is that between half and three quarters of the metal comparisons were not significant suggesting that most metals emissions were unaffected by the difference in fuels.

The following sections address the findings for each of the metals that produced significant differences.

Volatile Metals

Mercury [Hg]

Mercury is a volatile metal that would not be retained in the clinker in the same manner as most of the metals and would not be expected to correlate with difference in TSP emission rates. It is also unlikely that mercury levels would be greatly influenced by the isokinetic limitations of the 2019 LCF tests.

Geometric Mean [$\mu\text{g}/\text{Rm}^3$ @ 11% O ₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Mercury	3.8	4.0	6.2	1.8	3.9

The comparison of the Baseline tests was the only comparison of the 8 conducted that did not produce a significant difference statistic. As can be seen in the table, the 2019 LCF run was higher than the other tests and the 2020 LCF was lower than the other tests. European data indicates that the average of over 300

measurements from facilities was 20 ug/Nm³ suggesting that the Brookfield data is at the low end of typical measurements. There are no standards for mercury emissions from cement kiln emissions in Canada.

ReMAP data indicates that, at these measured concentrations, the range for single future tests would be 1.7 – 13.9 ug/m³. Thus, while the statistical tests suggest a difference between the tests, the stack levels overlap based upon method precision estimates. The differences may be related solely to the precision limits of the method. However, they could also indicate a difference in the mercury input to the process. The most likely source of mercury is the raw feed.

Considering these factors, low carbon fuel use is unlikely to affect mercury emissions.

Major Metals in Raw Meal

A group of five metals were found to have concentrations greater than 100 µg/Rm² @ 11% O₂:

Aluminum; Calcium; Iron; Magnesium; and Sodium

The feed to a cement kiln is generally a mix of limestone and clay with various additional materials added to meet the specific chemical requirements of the finished product. The BAT notes that limestone contains up to 96% calcium carbonate and aluminum oxide is a major constituent of both limestone and clay. Magnesium is the eighth most abundant element in the earth’s crust and might be expected to be found in the raw materials fed to the process. The BAT lists magnesium oxide at 0.1 to 5-6% in both limestone and clay feeds. Iron, Fe₂O₃, is added to facilitate the clinkering process. The Raw Meal chemical composition listed in the BAT identifies calcium oxide as 40-45% of the mass; silicon oxide at 12-16%; aluminum oxide at 2-5%; iron oxide 1.5-2.5%; magnesium oxide 0.3-5% and sodium oxide 0.1-0.5%. With these compounds varying in the raw materials that are blended to produce the raw meal, it is possible that some of the variability seen in the emissions is related to changes in the mix of materials in the raw meal.

For this discussion, these elements have been combined to examine significant means differences. The ReMAP method variability cannot be applied to these elements because the equation has not been validated for the concentration ranges measured. The results for 2017 Baseline did not include the 4 elements that are blank in the table below.

Geometric Mean [µg/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Aluminum		434	773	534	434
Calcium		5324	11398	7442	5343
Iron	150	377	433	397	238
Magnesium		162	249	308	162
Sodium		318	253	1543	318

Aluminum [Al]

The higher concentration measured for the 2019 LCF series resulted in significant mean value difference from the 2019 Baseline series only. As noted above, the finding could be the result of differences in the feed to the kiln. Since the 2020 LCF series was not significantly different than the 2019 Baseline, it could be concluded that LCF are unlikely to significantly affect aluminum emissions.

Calcium [Ca]

The statistical tests indicate that the 2019 LCF series had significantly different mean values for the 2019 Baseline. The 2019 LCF mean could be the result of differences in the raw meal composition, but as noted earlier, there is a positive correlation between calcium and TSP emissions indicating that changes in TSP levels may play a factor too. Since the 2020 LCF did not result in significant differences when compared to the 2019 Baseline, LCF are unlikely to influence calcium emissions.

Iron [Fe]

Iron was highest for the 2019 LCF series and lowest for the 2017 Baseline series. The means differences for the 2017 Baseline and both the 2019 Baseline and the 2020 LCF were statistically different but not with the 2019 LCF because of the high variability. Comparing either of the LCF series, 2019 and 2020, with the combined Baseline results indicates there is no reason to suspect the means are not the same. There is no statistical evidence that the LCF will change the iron emissions levels in a significant fashion.

Magnesium [Mg]

The results from the three series when magnesium was measured show the highest level was reported for the 2020 LCF testing, while the lowest values were from the 2019 Baseline. That low level produced a significant statistic when the comparison to the 2020 LCF was completed. However, the 2020 LCF results reported a significant amount of magnesium in the blank train sample, 145 $\mu\text{g}/\text{m}^3$ compared to 20 $\mu\text{g}/\text{m}^3$ suggesting that either there was contamination in the samples or that the laboratory results were biased high. The lack of a significant difference for the other tests suggests that the 2020 results may be misleading. There is no reason to suspect that the high levels in the 2020 testing were from the low carbon fuel.

Sodium [Na]

Sodium is a semi-volatile metal and will combine with chlorides and sulphates and the majority will be incorporated into the clinker. The table shows the 2020 LCF concentration to be the highest and the differences between the other two series were both significant.

A review of the laboratory results revealed that the blank train values were the same order of magnitude as the samples for all three series. This suggests that the differences, while statistically significant, may reflect material in the samples that did not originate from the stack. The comparison of the 2019 LCF result and the 2019 Baseline were not significantly different, suggesting little effect of low carbon fuels on sodium emissions.

Semi-Volatile Metals

In addition to sodium discussed above, there were four metals included in the list of metals analysed that are classified as having semi-volatile behaviour:

Antimony; Cadmium; Selenium; and Zinc

As explained in the BAT these metals or their compounds condense as sulphates or chlorides at temperatures of between 700 and 900 C and inner circulation occurs in the kiln process. This results in these elements reporting to the clinker with only a limited amount being released in fine particulate matter that escapes the system. Since these elements are expected to behave in a similar manner they are discussed in this section.

Geometric Mean [µg/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Antimony		2.0	2.44	0.2	2.0
Cadmium	0.2	0.5	0.24	0.2	0.31
Selenium	2.8	4.5	2.51	1.7	3.7
Zinc	29.9	39.9	14.5	12.9	35.8

Antimony [Sb]

Imposing the substitution for BDL values on the antimony data for the 2019 and 2020 data produced the geometric means seen in the table above, however, the laboratory results for 2017 Baseline, 2019 Baseline, 2019 LCF were all BDL values and only the last test in the 2020 LCF series was above the DL. All the tests are like the blank train values. While the independent means tests produced significant statistics for the comparison of the 2019 tests; the LCF tests; and the 2019 Baseline to the 2020 LCF test, these are artifacts of the substitution approach. Given that only one of 12 test cases produced a laboratory result above the detection limit, the statistical uncertainty associated with the means test is likely very high. The low concentrations do not allow the ReMAP approach to be used to determine if variability in the measurement procedure was a factor in the T3MP 2020 test value.

Given the low levels and the largely BDL results, it can be assumed that there is no effective difference in the antimony emissions for the tests.

Cadmium [Ca]

Cadmium was one of the metals used for the ReMAP study, however the values in this report are below the lower end of the range used to develop the Cd power function relationship. The lower end of the average values used for ReMAP was 1.38 ug/m³ at which level the 4 tests included had a bias corrected RDS of 71%. This suggests that there is potential for a wide variability at low cadmium levels. Differences were identified for 2017 vs 2019 Baseline; 2019 Baseline vs 2019 LCF; and 2019 Baseline and 2020 LCF. The 2019 Baseline values were higher, but it is likely that all the results cover the range of values that would be expected from the method.

Laboratory detection levels influenced the results, and likely created artifacts during the means comparison. The DL for 2017 was 0.18 ug; for 2019 the nitric digest had the same DL while the HF digest DL was 0.36 and

the back half was 0.23 or 0.09. The 2020 laboratory results reported DL at 0.1 ug for the digests and 0.05 for the back half samples. The 2020 test had all nitric and back half sample volumes above the DL and 1 on the HF results was above the DL. Only 2 nitric digest results were above the DL in the 2019 testing. All 2017 results were BDL. DL substitutions created artifacts for the 2019 data that likely influenced the statistical tests.

Given that the data appears to move with the detection limit, and that uncertainty at the levels measured is high, there is insufficient data to suggest that there is any effective difference in cadmium emissions.

Selenium [Se]

Selenium was included in the Method 29 validation trials but there was insufficient data to include it in ReMAP. The statistical tests suggest that the 2019 series had different means and the LCF tests comparison produced significant statistics as did the comparison of Baseline 2019 to LCF 2020. The DL for 2017 was 2 ug the same as the nitric digest for the other series. The HF DL was 2 ug for 2020 and 4 for 2019 while the back half DLs varied from 1 (2020), 3.5 (2019 LCF) and 10 (2019 Baseline). The 2019 tests had nitric results all above the DL, while none of the HF digests were above the DL and only 1 Baseline back half value was above the DL. The 2020 LCF series had 1 nitric and 3 back half results above the DL. The change in the DL for the tests will produce artifacts in the means comparison. The lower 2020 results being with the lowest BH detection limit.

Average concentrations found during the Brookfield testing are in the range for application of the ReMAP combined metals approach and indicate that single test results would overlap for all the combinations of series compared. This suggests that the statistical differences are a function of the variability of the sampling method and not a function of the application of low carbon fuels.

Zinc [Zn]

The 2017 Baseline values were limited due to 2 BDL values and comparisons could not be made to the 2019 or 2020 series. Comparisons between the 2020 LCF and both the 2019 Baseline and the combined Baseline data were significant. However, this statistic would appear to be driven by the substitution process because the back half samples for the 2019 Baseline were all BDL but were reported as 50; 100; and 250 ug. The DLs for the 2019 LCF similar to the 2019 Baseline values, but the back half DL value was 13 ug. The 2020 DLs were 6 for both acid digestions and 3 for the back half sample.

Looking at the comparisons involving the 2019 Baseline, the ReMAP analysis shows that the 2019 Baseline series is different from the 2020 LCF series. The artifact created by the DL substitution likely explains this result; the 2019 Baseline results are likely outliers. Since there was no significant statistic for the other comparisons, low carbon fuel is likely to have no effect on zinc emissions.

Refractory or Non-Volatile Metals

For convenience, the discussion for these metals is split into different concentration ranges.

Low Concentration Trace Metals [less than 2 ug/Rm³ @ 11% O₂]

The lowest concentrations measured for non-volatile metals were recorded for the 6 elements in the following table.

Geometric Mean [µg/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Arsenic	0.5	1.8	1.13	0.7	0.94
Beryllium		0.35	0.19	0.15	0.35
Bismuth	0.26	1.03	0.62	0.33	0.52
Cobalt	0.2	0.5	0.31	0.38	0.31
Silver	1.8	1.4	0.39	0.3	1.60
Tellurium		0.82	0.88	1.13	0.82

For the 2017 Baseline BDL values result in the absence of Beryllium and Tellurium values.

Arsenic [As]

Arsenic is an element that was validated for Method 29 and it was one of the elements examined in the ReMAP study. The 2019 Baseline produced the highest geometric mean and that series was identified to have significant statistics when compared to the 2017 Baseline and the 2020 LCF series. Detection limits may play a role in the reported results due to the substitution procedure. For the 2019 Baseline/2019 LCF/2020 LCF tests the DL for the HF digestion was 1.6/1.6/1.0; for the HNO₃ digestion it was 0.8/0.8/1.0 and the back half was 0.4/1.0/0.2. The HF digestion did not provide any detectable results, the back half had only one result above the DL for the 2020 LCF series, and the HNO₃ results were above the DL for all cases used for 2019 LCF (2) and 2020 LCF (3) tests, and 2 of the 2019 Baseline cases.

ReMAP calculations suggest that the differences seen are within the range expected from the method, suggesting that the differences are not meaningful changes in emissions. Based upon this finding, there is no difference in arsenic emissions.

Beryllium [Be]

Beryllium sampling using Method 29 has been validated and Beryllium was one of the metals addressed by ReMAP. The geometric mean for the 2019 Baseline was the highest and statistics were significant when that series was compared to either of the other series, however all the data were BDL with the exception of one back half test in the 2020 LCF series. The 2019 Baseline series had the highest detection limit for the back half sample and this drives the geometric mean values.

While statistical differences were identified the differences are the result of the substitution approach and the detection limits varying. There is no reason to assume that there is any difference between beryllium emissions regardless of the fuel used.

Bismuth [Bi]

Bismuth comparisons were significant for the comparison 2019 Baseline comparison to the 2020 LCF series and the two LCF series. Bismuth is an element that was not validated for Method 29. Reviewing the laboratory data only the 2017 data produced values above the DL, and the 2019 Baseline detection limits were the highest so the substitution procedure accounts for the differences. The sum of DL values were 0.6/4.4/2.55/1.1 for the series, and these reflect the results of the statistical analysis.

Bismuth differences are due to analytical differences for the series and there is no difference in emissions.

Cobalt [Cob]

The Baseline series comparison produced a significant difference as did the comparison between 2019 Baseline to 2019 LCF series. The 2019 Baseline was the highest values which arose from the nitric digestion. All three series had nitric digestion values above the detection limit. The uncertainty in cobalt measurements identified by the ReMAP combined metals regression indicates that the results of the tests overlap.

Since the results from all series are expected to overlap on the basis of the ReMAP evaluation, it is difficult to assign the differences to the effect of low carbon fuel use.

Silver [Ag]

Silver is an element that was validated for Method 29. Significant silver mean differences were identified for both the Baseline comparisons to the 2020 LCF data. The high variance in the comparisons with the 2 cases in 2019 LCF resulted in insignificant t-statistics for comparisons to this series. All series had results above the detection limit for the nitric digestion, however the 2020 LCF detection limits were the lowest and the results were the lowest.

The uncertainty in silver measurement identified with the ReMAP combined metals analysis shows that the higher concentrations would cover the range reported for the lower concentrations suggesting that all the data is likely within the measurement variability. While the statistics are significant, the variability suggests that there is no difference in the results as a result of lower carbon fuel use.

Tellurium [Te]

Method 29 was not validated for Te. The majority of the tellurium measurements reported by the laboratories were below the detection limit. The 2017 Baseline was eliminated due to BDLs but the substitution meant that the other 3 series had values, albeit the differences in the values were related more to the detection limits reported by the laboratories than actual measurement data. The only comparison with significant statistics was the 2019 Baseline and the 2020 LCF series and the 2020 LCF was higher. The DL for the HNO₃ digests were 2 ug/2ug/1.5ug for 2019 Baseline/2019 LCF/2020 LCF respectively. The HF digestion DL was 1/1/1.5 and the back half DL was 0.5/0.5/0.75. The elevated detection limits for the HF digestion and the back half sample for the 2020 LCF series elevated the geometric mean resulting in the higher levels.

The statistical differences identified for Tellurium reflect the laboratory detection limits and thus there is no difference between the data regardless of fuel.

Medium Concentration Trace Metals [greater than 2 and less than 20 µg/Rm³ @ 11% O₂]

A group of 3 non-volatile metals were identified with next lowest concentrations. Unlike the previous group, there were no elements where substitution for BDL results created anomalies in the data. Indeed, all results were at reportable levels for the front half digestions and all back half results were BDL, although well below the front half levels.

Geometric Mean [µg/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Molybdenum	3.4	7	5.8	7	4.9
Strontium	2.9	8.4	17.6	10.3	4.9
Manganese	11	14.4	19.4	19.5	12.5

Molybdenum [Mo]

Insufficient molybdenum data did not allow this element to be included in the Method 29 validation studies. The low values in the 2017 Baseline resulted in comparisons with the other tests, 2019 Baseline, 2019 LCF and 2020 LCF having significant t-statistics. The uncertainty in molybdenum measurements identified by the ReMAP combined metals regression suggests that all the runs overlap.

While statistical differences were identified for Molybdenum the results are all within the ranges of values that can be explained by the measurement precision associated with those levels. There is no reason to assume that there is a significant effect from low carbon fuel use.

Strontium [Sr]

Strontium was not included in the US EPA validation of Method 29. The data in the table shows a large variation. This results in the identification of significant differences for the 2017 Baseline versus each of the other test series, as well as significant differences for both the comparison of the 2019 series and the comparison of the LCF series. Applying the ReMAP formula reveals that the 2017 Baseline data lies outside the measurement variability of the other series, as does the 2019 LCF series.

Given that the 2019 Baseline and the 2020 LCF are not statistically different it could be that the element is in the raw feed. Strontium is a common element found in sedimentary parts of the earth's crust at levels of 370 ppm, variations in the raw meal could explain the differences. Moreover, as noted earlier, strontium is one of the elements that was positively correlated to TSP emissions. These explains are more plausible and would lead to the conclusion that there is little influence on strontium emissions when using low carbon fuels.

Manganese [Mn]

Manganese is an element that was validated for Method 29. The 2019 LCF data produced significant statistics when compared to the Combined Baseline data. That comparison is limited by two widely separated result associated with the 2019 LCF tests. The ReMAP evaluation shows that all the data points overlap suggesting that method variability is a factor in the statistical differences.

Given the measurement precision findings there is no reason to assume that there is a significant effect from low carbon fuel use.

Highest Concentration Trace Metals [greater than 20 and less than 100 µg/Rm³ @ 11% O₂]

A final group of metals are shown in the table below. Unlike the elements with lower concentrations there is no series that had all the higher values.

Geometric Mean [µg/Rm³ @ 11% O₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Barium	21.8	26.4	23.0	12.4	23.99
Boron	67.8	59.2	31.2	124.1	63.3
Phosphorus		154.8	92.6	67.6	154.8
Tin	35.4	45.1	8.7	27	39.9
Titanium	8.7	18.1	38.5	15.9	12.5

Barium [Ba]

Barium is an element that was validated for Method 29. The 2020 LCF comparison to the other series all produced significant t-statistics likely related to the low concentration reported for 2020. The uncertainty in the barium measurement identified in the ReMAP combined metals analysis produces no overlap for the comparisons with the 2020 LCF series suggesting this result is different.

The 2020 LCF results appear to be an anomaly. The fact that there is no statistical difference between the other series suggests that LCF will have little influence on barium emissions.

Boron [B]

Boron is an element that was not validated for Method 29 and results are subject to interferences from the sampling train components. In particular, the front half HF digestion of the sample has the potential to produce measurable boron masses. Borosilicate glass has been noted by the US EPA to lead to interference with boron measurements in water samples¹¹. The 2019 LCF results were all BDL for the blank train and the samples. The front half results for the 2020 LCF had a blank train level similar to the sample results: 322 ug versus 337/343/403 ug. The back half results for 2020 LCF were BDL at 10 ug for the blank train and 30.6/19.8/17.5 ug for the samples. The 2019 Baseline results had a nitric front half BDL at 30 ug for the blank and the samples while the HF front half results were blank of 20 ug and 45/68/109 ug for the samples. The back half blank was BDL at 15 ug while the BH samples were BDL at 150 ug. For completeness, the blank for 2017 Baseline was BDL at 30 ug while the samples were 507/154/348 ug.

Substitution for the BDL values for the 2019 LCF tests distorts the comparisons and is not appropriate. Only the 2017 Baseline versus the 2020 LCF are directly comparable because BDL substitutions are not present in either result, but the 2017 had a large variance too. There was no statistical significance to the means in this case. The 2019 Baseline HF digestion results were approximately 20% of those for 2020 LCF runs. Matched with the BDL values for the 2019 LCF runs it suggests that the laboratory procedure was different for these tests.

¹¹ https://www.epa.gov/sites/production/files/2014-09/documents/chapter_3_boron.pdf

Borates may be in the feed to the kiln. The EPA report notes that elemental boron is not found in nature, but borates are natural and ubiquitous. Borates are most predominantly found in nature in oceans, sedimentary rocks, coal, shale, and some soils. While changes in the concentration of boron in the raw meal is a possible explanation, the differences in the analytical is a more likely explanation.

Discarding the influence of the substitutions for the 2019 testing, the comparable means for the 2020 LCF and 2017 Baseline tests suggests that there is no reason to suspect a change in fuel will result in differences in boron emissions.

Phosphorus [P]

Phosphorus was not included in the Method 29 validation studies. Phosphorus data for all the test series were below the laboratory detection limit, thus the data in the table reflects the variation in the detection limits determined for the various analytical runs. While the application of the independent means test produced significant statistics for the 2020 LCF series when compared to both other series and the 2019 Baseline series produced a significant statistic for the 2019 LCF series, these are solely the result of the detection levels.

No conclusions can be drawn from the phosphorus results given the element was not quantified.

Tin [Sn]

Tin was not included in the US EPA validation of Method 29. The low value for the 2019 LCF series resulted in significant statistics in comparisons to the 2017 Baseline, 2019 Baseline and 2020 LCF. In addition, the 2019 Baseline produced a significant statistic in the comparison to the 2020 LCF series. Both LCF series have significant statistics when compared to the combined Baseline data.

Given the range of data from the tests the combined metals statistics from ReMAP can be used. The 2019 LCF series results do not overlap the data from the other tests, suggesting that the difference is real. The Baseline comparisons overlap, and the 2020 LCF results are at the low end of their expected range.

The mixed response of the LCF series suggests that there is limited evidence to suggest that there were any effects on tin emissions from the use of low carbon fuels.

Titanium [Ti]

Titanium is included in the Method 29 validation studies. The 2019 LCF series had the highest value and this resulted in significant statistics when compared to the other series. In addition, the 2017 Baseline produced significant statistics in the comparisons with the 2019 Baseline and the 2020 LCF series.

Regardless of the series examined, blank train values were in excess of 30% of the average of the stack emission results and the blank train for the 2019 LCF series (19.5 $\mu\text{g}/\text{Rm}^3$ @ 11% O_2) was similar to the geometric mean values reported for the other tests. The BAT document suggests that TiO_2 is typically found in most of the raw materials fed to the kiln. Titanium was another element found to correlate with the TSP emissions which could be another reason for the variation in the results.

Applying ReMAP the 2019 LCF values are outside the range expected from method variability whereas the other series had ranges that overlap indicating that some of the reported differences were the result of measurement precision.

The fact that the 2019 Baseline and the 2020 LCF series show no significant differences suggests that, even with the other data, the use of LCF had little impact on titanium emissions.

Metals producing no Significant Statistic for the Mean Difference

Comparisons were run for all the metals listed in Table 1. The calculations did not produce statistics indicating that there were any differences between the mean values for the metals shown below.

Geometric Mean [$\mu\text{g}/\text{Rm}^3$ @ 11% O_2]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Lithium	5.9	8.1	8.4	4.8	6.9
Nickel	7.3	8.3	4.1	4.4	7.77
Lead	27.2	31.2	26.1	24.1	29.2
Thallium	14.0	32.3	32.1	23.8	21.3
Silicon	-	520	1348	492	520
Chromium	4.72	12.5	4.5	4.93	7.67
Copper	2.22	4.79	2.36	4.22	3.26
Vanadium	3.13	3.09	2.3	2.68	3.11

In most instances the data for these elements resulted in high variances between the data, and this results in reductions in the value of the t-statistic significance, that is the significance exceeded the 0.05 criteria. Given this finding, it can be concluded that changes in the fuel mix at the facility had no effect on emissions of these metals.

Organic Species

The US EPA¹² states that an organic compound is any of a large class of chemical compounds whose molecules contain carbon. A few compounds such as carbonates, simple oxides of carbon and cyanides, as well as the allotropes of carbon, are considered inorganic, even though they contain carbon. Distinguishing between organic compounds is usually done by looking at the compound's volatility as an indicator of its vapor pressure. Volatility is a tendency of a substance to vaporize or the speed at which it vaporizes. Substances with higher vapor pressure will vaporize more readily at a given temperature than substances with lower vapor pressure. Since the volatility of a compound is generally higher the lower its boiling point [BP] temperature, the volatility of organic compounds is sometimes defined and classified by their boiling points. Organic compounds can be divided into semi-volatile compounds [SVOCs] and volatile compounds [VOCs].

Different sampling procedures are required to sample VOCs and SVOCs. US EPA Method 23 provided results for the SVOCs: PCDD/F; PAHs; Chlorobenzenes; Chlorophenols; and Polychlorinated Biphenyls. US EPA Method 30, known as the VOST method, is used for VOCs with a BP<100 C; the tedlar bag grab sample approach for Principal Organic Hazardous Constituents [POHC] with BP<121 C; while chilled impinger techniques were used for alcohols and aldehydes.

The independent means t-test was run for three series of SVOC tests: 2017 Baseline; 2019 Baseline and 2020 LCF. VOC comparison tests were completed for 2017 Baseline; 2019 Baseline and 2020 LCF. No VOC testing was done in 2020. A total of 8 PAHs had results that produced significant t-statistics for the 2019 Baseline versus 2020 LCF series only; 4 polychlorinated biphenyl comparisons were identified as producing significant statistics; and 7 VOC compounds were found to have significant means difference statistics. While the results tables at the end of the report show some PCDD/F congeners and homologues produced t-stats that were significant, the KMTEQ_{WHO2005} comparison is the only one considered in this discussion. Many of the congeners and homologues in the other tests were found to have BDL results and thus comparisons of these are of limited value. Comparison for many of the compounds were limited by the presence of BDL values, or the fact that the laboratory results did not consistently list all organics.

The uncertainty associated with the precision of monitoring of organic species has not, with the exception of PCDD/F data, been assessed in the same way as it has for metals, particulate and hydrogen chloride emissions in the ReMAP study. Thus, is it not possible to provide statistically derived ranges for organics results for other than PCDD/F.

The BAT notes that:

In heat (combustion) processes in general, the occurrence of volatile organic compounds (and carbon monoxide) is often associated with incomplete combustion. In cement kilns, the emissions will be low under normal steady-state conditions, due to the type of kiln used, the large residence time of the gases in the kiln, the high temperature, the nature of the flame (2000°C) and the excess oxygen conditions. These are process conditions where the organic compounds are decomposed and destroyed with a high efficiency rate (>99.9999%).

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¹² <https://www.epa.gov/indoor-air-quality-iaq/technical-overview-volatile-organic-compounds>

... emissions of volatile organic compounds (VOCs) can occur in the primary steps of the process (preheater, precalciner), when organic matter that is present in the raw meal, is volatilised as the feed is heated. The organic matter is released between temperatures of 400 and 600°C. The VOC content of the exhaust gas from cement kilns typically lies between 1 and 80 mg/Nm³, measured as TOC. However, in rare cases emissions can reach 120 mg/Nm³ because of the raw material characteristics.

European Standard EN12619:2013 specifies that the measurement of TOC is completed with a flame ionization detection [FID] system. Continuous FID measurements could provide comparable data but were not used for the 2020 series of tests. In 2019 the LCF tests the average THC level was 6.2 mg/m³ whereas the 2019 Baseline average was 7.8 mg/m³. The values are similar to those found in large scale European testing. The means comparison found no significant difference between Baseline tests, or Baseline versus LCF test results.

The discussion of organic compounds that were identified to have significant differences between the series mean values is divided into groups of compounds: PAH; CB and PCB, Volatiles and PCDD/F.

Polyaromatic Hydrocarbons [PAH]

The PAH compounds listed in the laboratory reports varied by series, but as can be seen in the table below there were quantifiable amounts of the compounds identified for most of the series. The -ve sign in the table indicates missing data because values were below the detection limit for these compounds for both tests in the 2017 series. Only 2 samples were submitted to the laboratory for the 2017 series. The table shows 9 of the 45 PAH compounds that were identified to have significant mean differences. The first 8 relate to the comparison of 2019 Baseline data to the 2020 LCF data. The last compound, benzo(e)pyrene, produced significant statistics for the Baseline comparison. Other comparisons to the 2017 Baseline were compromised by large variances in the values for the two cases available for the test series.

Geometric Mean [µg/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2020 LCF	Combined Baseline
Naphthalene	74.5	55.8	169	62.6
Acenaphthylene	2.6	2.0	3.3	2.23
Acenaphthene	0.58	0.27	0.15	0.37
Phenanthrene	10.1	10.9	8.42	10.54
Benz(a)anthracene	0.21	0.13	0.21	0.16
Benzo(a)pyrene	-	0.085	0.032	0.084
Indeno(1,2,3-cd)pyrene	-	0.03	0.016	0.031
1-Methylnaphthalene	-	8.7	14.8	8.66
Benzo(e)pyrene	0.56	0.70	0.59	0.63

There does not appear to be a consistent trend in high/low levels in any series although there appears to be some groupings of compounds that had significant differences. Unlike TSP, metals, and PCDD/F there was insufficient data for the ReMAP study to assess the precision of the sampling methods for PAHs. Since PAHs and PCDD/F are sampled using the same equipment and analysed from the same samples, one might be tempted to say that the power law relationship for PCDD/F could be applied. However, ReMAP PCDD/F

metrics are based upon either sum of the homologues of these compounds or the sum of the toxic congeners and such data is not available for PAHs.

Naphthalene [NAPHTHENE]

Naphthalene is typically derived from coal tar but can be found naturally in the environment¹³ and is created by cigarettes and automobile exhaust among other combustion sources. The significant means comparison statistics occurs for the conditions where the naphthalene emissions were higher for the 2020 emissions case.

Acenaphthylene [ACENPHLN]

A member of the naphthalene class, acenaphthylene is a PAH most commonly found in coal tar, coal tar pitch, bitumen and asphalt. It can be found in soot and products of incomplete combustion. Similar to the naphthalene results, the 2020 LCF emissions were higher than the 2019 Baseline values.

Acenaphthene [ACENATHN]

Another member of the naphthalene class, the literature suggests that combustion sources can release acenaphthene, and it can be found in coal tar and similar products. The 2020 LCF series had the lowest geometric mean unlike the two PAHs discussed previously.

Phenanthrene [PHENATHN]

This compound is a member of the phenanthrene family since it contains a tricyclic aromatic compound with three non-linearly fused benzene rings. However, like acenaphthene, the 2019 Baseline mean was larger than that for the 2020 LCF series.

Benz(a)anthracene [BENZANTH]

A member of the phenanthrene family of compounds, the geometric mean for the 2017 Baseline and the 2020 LCF runs were the same. The 2019 Baseline was lower, and significantly different from the 2020 LCF value. The means may differ, but the fact that one set of Baseline data is the same as the 2020 LCF series leads to speculation that the 2019 Baseline values were low.

Benzo(a)pyrene [BNZAPYRN]

A member of the pyrene class and found in cigarette smoke, analytical results are only available for the 2019 Baseline and 2020 LCF tests. The data would suggest that the 2020 LCF runs were lower; but, given the variability in the three runs for each of the series, the conclusion might be speculative.

Indeno (1,2,3-cd)pyrene [INDEPYRN]

This compound is another in the pyrene class. Only one comparison is available and it was significant, with the 2020 LCF result being lower than the 2019 Baseline value.

1-Methylnaphthalene [MTLHAPH1]

A compound in the naphthalene class, this compound is found in black walnut¹⁴ indicating that it might exist in nature. Having a low boiling point, it could be released from the raw meal. The mean for the 2020 LCF

¹³ <https://www.canada.ca/en/health-canada/services/chemical-substances/challenge/batch-1/naphthalene.html>

¹⁴ [T3DB: 1-Methylnaphthalene](#)

series was nearly twice that of the 2019 Baseline test and produced significant statistics.

Benzo(e)pyrene[BENZEPYRN]

Another member of the pyrene class found in incomplete combustion situations. The nearly identical geometric means for the 2017 Baseline and the 2020 LCF suggests little effect of different fuels, yet the 2019 Baseline produced the significant difference statistic.

The table shows that there is no consistency in the concentrations reported for the different PAHs, some compounds are higher for the LCF series some for the Baseline series. Literature reports reporting on the sampling of PAHs from other combustion sources and the ambient environment suggest that the nature and the size of particulate matter in the sampling zone appears to influence the quantity and speciation of the PAHs collected. This could be a factor with the data reviewed for this study. Considering the data, it is not possible to categorically state an effect from changing fuel in the kiln.

Polychlorinated Biphenyls [CBP]

There are 209 polychlorinated biphenyls (PCBs). PCBs are a group of synthetic organic compounds with 1-10 chlorine atoms attached to biphenyl. They were manufactured as commercial mixtures but banned in the 1970's because they were found to bioaccumulate and cause harmful health effects. However, PCBs do not break down readily and are still found in the environment.¹⁵ Comparisons were completed for the homologues of PCBs, the 10 groups with different chlorination levels, rather than dealing with all the congeners. The laboratory quantified the 2020 homologues in the 0.01 – 12 ng range, whereas the congener samples were present at 0.5 pg or less with numerous BDL values.

WHO¹⁶ suggests that indoor levels of PCBs (total) below 300 ng/m³ are of no concern. The majority of the PCBs in the samples analysed for this study are monochlorinated, which are more volatile. The percentage of monoPCB versus the total PCB was 79% in 2017 versus the LCF values of 88% in 2019 and 91% in 2020. It should be noted that monoPCB was not quantified in the 2019 Baseline results when the sum of the other PCB was less than 10 ng/m³. The dashes in the table indicate all tests were BDL. As the chlorination level increased the concentrations generally decreases as seen in the table.

Geometric Mean [ng/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2020 LCF	Combined Baseline
Dichlorobiphenyl	40.5	-	18.7	40.5
Trichlorobiphenyl	5.31	3.14	2.55	3.37
Tetrachlorobiphenyl	10.74	2.24	1.06	4.19
Pentachlorobiphenyl	2.20	1.94	0.56	2.04
Hexachlorobiphenyl	1.01	0.61	0.22	0.75
Heptachlorobiphenyl	0.18	0.06	0.05	0.096
Octachlorobiphenyl	-	0.009	0.0122	0.009
Nonachlorobiphenyl	-	0.003	0.015	0.003
Decachlorobiphenyl	-	0.006	0.062	0.006

¹⁵ [Polychlorinated Biphenyls \(PCBs\) | Toxicological Profile | ATSDR \(cdc.gov\)](#)

¹⁶ [Microsoft Word - 5.10-PCBs.doc \(who.int\)](#)

Only 4 homologues of PCBs produced significant statistics for the mean comparison between the 3 series shown in the table above:

- The comparison of 2017 Baseline and 2020 LCF for trichlorobiphenyl.
- The 2019 Baseline versus the 2020 LCF for hexa, nona and deca PCBs.

The trichlorobiphenyl homologue was one of two PCB homologues that was correlated with TSP emissions. Another observation for this compound was that the 2019 Baseline results produced a large variance, likely reducing the significance of any difference in the means test, and the blank train for this test series was the high of the acceptable series. The LCF series had a lower geometric mean. The 2019 Baseline results were also higher than the 2020 LCF series for hexachlorobiphenyl. However, both the nona and deca PCBs 2020 LCF results were higher than the 2019 Baseline data. The latter homologues were BDL values in the 2017 Baseline tests. The nonaPCB detection limit for 2017 series was similar to the levels recorded in 2020 LCF. Generally, the concentration of the emissions of the homologues follows the trend of the blank trains suggesting method precision might be a factor in the reported values.

While the variability of the results suggests that there might be limitations in the data, the lower 2020 LCF results compared to the 2019 Baseline and the 2017 Baseline suggest that for the 2020 series the use of low carbon fuels may have led to reduced emissions of all but the octa, nona and decaPCBs.

Volatile Organic Compounds

Ethylbenzene [ETHBENZ] and o-Xylene[XYLENEO] Sum of m-Xylene and p-Xylene [XYLENEMP]

Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are discussed in the BAT which notes that the range of these compounds emitted in European cement kilns is 20 – 3600 ug/m³. Furthermore, the BAT states that BTEX emissions are not dependent on the fuels used, rather it is likely that these emissions are due to changes in the raw material feed.

These volatile compounds are part of the same family and were quantified using the VOST method. That method was not employed for the 2020 LCF test series so there is no data.

Geometric Mean [$\mu\text{g}/\text{Rm}^3$ @ 11% O ₂]	2017 Baseline	2019 Baseline	2019 LCF	2020 LCF	Combined Baseline
Ethylbenzene	54.4	37.1	26.7	-	45
m-Xylene + p-Xylene	109.8	75.1	58.1	-	91
o-Xylene	49.6	32.1	23.1	-	40
N-Hexane	39.8	51.4	79.8	-	45
Heptane	34.9	26.5	29.4	-	30
Propene	1812	1428	1364	-	1609

Significant statistics were produced by the comparison of the 2017 to 2019 Baseline for m-,p- xylene and o-xylene. Significant statistics were also found for the ethylbenzene and m-, p- xylene for the 2017 Baseline versus the 2019 LCF series and for the comparison of the 2 2019 series. The o-xylene comparisons were

influenced by 2 BDL values for 2019 LCF. The presence of a BDL value for ethylbenzene in 2019 LCF may also play a part in the comparison.

The variations are most likely the result of changes in the materials in the raw meal as noted in the BAT. The 2019 LCF tests did produce the lowest concentrations for each of the compounds.

n-Hexane [HEXANEN], Heptane [HEPTANE] and Propene [PROPENE]

The chemicals n-hexane and heptane are solvents. N-hexane can be found in gasoline. Heptane is a non-polar solvent used in laboratories and is also known to be a plant metabolite. Propene is a gas, sometimes used as a refrigerant, with a boiling point of approximately -50 F. These chemicals were collected using tedlar bag samples since they evaporate easily.

Comparing the means identified significant statistics for all three chemicals for the 2017 Baseline to the 2019 LCF series, but no other significant statistics were identified. It should be noted that the 2019 LCF results were only available for 2 of the 3 runs so the comparisons, performed with fewer cases, should be considered weak. As with the BTEX compounds the differences in the comparisons are most likely related to the raw feed.

Polychlorinated dibenzo-p-dioxins and Polychlorinated dibenzofurans [PCDD/F]

A total of 17 congeners and the tetra through octo homologues of these compounds are routinely analysed to determine emissions. As discussed earlier, the congeners are weighted by their relative toxicity and the sum of the weighted values is referred to as the toxic equivalent for PCDD/F. For this study, the WHO₂₀₀₅ weighting was applied. The ReMAP study examined the precision of Method 23 based upon both the TEQ values and the sum of the homologues (the total PCDD/F). The latter was the basis of regulatory standards in the US at the time of the study. TEQ have long been the reference for regulatory standards in Canada and Europe.

As discussed in Appendix A, the presence of non-detects in the PCDD/F congeners does not present a statistical hurdle for the determination of the TEQ values if the Kaplan Meier approach proposed by Helsel is applied. That is the approach used for this study. With the ReMAP precision assessment the KMTEQ_{WHO} mean differences can be examined with respect to whether they are the result of measurement imprecision, or if there is another reason for the finding. Without specific precision estimates for the individual congeners and homologues, it is not possible to comment on measurement related differences found for these compounds.

Geometric Mean [µg/Rm ³ @ 11% O ₂]	2017 Baseline	2019 Baseline	2020 LCF	Combined Baseline
PCDD/F TEQ by WHO ₂₀₀₅	50.71	16.95	6.40	26.28

PCDD/F have been designated as Track 1 substances by Environment Canada¹⁷. Track 1 substances are persistent, bioaccumulative, and anthropogenic. Virtual elimination from the environment of the Track 1 substances is one of the objectives of the Toxic Substance Management Policy developed by EnvCan. To provide guidance on virtual elimination, a Level of Quantification (LoQ) was suggested as the basis for a target emission concentration for air emissions. The LoQ for PCDD/PCDF was estimated to be 32 pg/m³ TEQ.

¹⁷ [ARCHIVED - LOQ for Air Emissions - Management of Toxic Substances \(ec.gc.ca\)](https://www.ec.gc.ca/archived-locq-for-air-emissions-management-of-toxic-substances)

The policy¹⁸ puts the onus on those who generate or use a Track 1 substances to demonstrate that the substance will not be released into the environment in measurable concentrations at any point in its life cycle. By setting limits based upon the lowest concentration of a substance that can be accurately detected and quantified using sensitive but routine analytical methods, virtual elimination does not mean chasing down that substance to its last molecule. With all tests conducted at Brookfield since 2019 are below 32 pg TEQ/m³ indicating that they are below the LoQ and satisfy the criteria that PCDD/F emissions be eliminated.

The independent comparison of KMTEQ_{WHO} means test identified statistical differences between each of the possible comparisons: 2017 Baseline to 2019 Baseline; 2017 Baseline to 2020 LCF; and 2019 Baseline to 2020 LCF. As discussed for metals, the ReMAP study provides a method to address the expected variation in values from stack testing. Early ReMAP evaluations did not contain a wide range of TEQ data but using the same methodology with a larger data base a study¹⁹ found the relationship between the concentration and standard deviation of the ITEQ listed in the table at the beginning of Appendix B was produced.

When the ReMAP relationship is applied, the 2017 Baseline results were outside the measurement precision range. This series contained only 2 values that were widely separated. It is worth noting that there were no BDL values in the 2017 congener results while 8 of the possible 51 congener values in the 2019 Baseline were BDL and over 68% of the congener values in the 2020 testing were BDL values. The data indicates that there could be a difference between the results attributable to the change in fuels with the LCF runs being lower.

¹⁸ [Track 1 substance: virtual elimination from the environment - Canada.ca](#)

¹⁹ J. Davis, A. Pollard and A. J. Chandler, "Comparison of variability in dioxin and furan data acquired using single train and simultaneous multiple train stack sampling methods," *Journal of the Air and Waste Management Association*, vol. 64, no. 10, pp. 1093-1101, 2014.

Data Tables

Table 1 List of Parameters recorded during Brookfield Testing

Table 2 Brookfield Test Results

Independent Means Test Results (unnumbered)

1. Independent Samples Test Comparison of Baseline 2017 vs Baseline 2019
2. Group Statistics of Baseline 2017 vs Baseline 2019
3. Independent Samples Test Comparison of Baseline 2017 vs LCF 2019
4. Group Statistics of Baseline 2017 vs LCF 2019
5. Independent Samples Test Comparison of Baseline 2017 vs LCF 2020
6. Group Statistics of Baseline 2017 vs LCF 2020
7. Independent Samples Test Comparison of Baseline 2019 vs LCF 2019
8. Group Statistics of Baseline 2019 vs LCF 2019
9. Independent Samples Test Comparison of Baseline 2019 vs LCF 2020
10. Group Statistics of Baseline 2019 vs LCF 2020
11. Independent Samples Test Comparison of LCF 2019 vs LCF 2020 vs LCF 2020
12. Group Statistics of LCF 2019 vs LCF 2020
13. Independent Samples Test Comparison of LCF 2019 vs combined Baseline 2017 & Baseline 2019
14. Group Statistics of LCF 2019 vs combined Baseline 2017 & Baseline 2019
15. Independent Samples Test Comparison of LCF 2020 vs combined Baseline 2017 & Baseline 2019
16. Group Statistics of LCF 2020 vs combined Baseline 2017 & Baseline 2019

Table 1 List of Parameters Recorded for Brookfield Tests

TESTDATE	Month Year of Test	Units
SAMPLEID	Description	
TEST	Test Run 0=Blank	
Year	Year	
Series	Within Year 1 Baseline 2 Trial Burn	
SMPLOC	Sample Location 1 Stack 2 Breeching	
Common Compounds		
TSP	Total Suspended Particulate	[mg/m3@11%]
CO	Carbon Monoxide	[mg/m3@11%]
NOX	Oxides of Nitrogen	[mg/m3@11%]
SOX	Oxides of Sulphur	[mg/m3@11%]
HF	Hydrogen Fluoride	[mg/m3@11%]
NH4	Ammonium	[mg/m3@11%]
CL2	Chlorine	[mg/m3@11%]
HCl	Hydrochloric Acid	[mg/m3@11%]
THC	Total Hydrocarbons	[mg/m3]
PM2.5	Particulate Matter <2.5 µm	[mg/m3@11%]
PM10	Particulate Matter <10 µm and >2.5 µm	[mg/m3@11%]
Metals		
HG	Mercury	[ug/m3@11%]
AL	Aluminum	[ug/m3@11%]
SB	Antimony	[ug/m3@11%]
AS	Arsenic	[ug/m3@11%]
BA	Barium	[ug/m3@11%]
BE	Beryllium	[ug/m3@11%]
B	Boron	[ug/m3@11%]
BI	Bismuth	[ug/m3@11%]
CD	Cadmium	[ug/m3@11%]
CA	Calcium	[ug/m3@11%]
CR	Chromium	[ug/m3@11%]
COB	Cobalt	[ug/m3@11%]
CU	Copper	[ug/m3@11%]
FE	Iron	[ug/m3@11%]
PB	Lead	[ug/m3@11%]
LI	Lithium	[ug/m3@11%]
MG	Magnesium	[ug/m3@11%]
MN	Manganese	[ug/m3@11%]
MO	Molybdenum	[ug/m3@11%]
NI	Nickel	[ug/m3@11%]
P	Phosphorus	[ug/m3@11%]
SE	Selenium	[ug/m3@11%]
SI	Silicon	[ug/m3@11%]
AG	Silver	[ug/m3@11%]
NA	Sodium	[ug/m3@11%]
SR	Strontium	[ug/m3@11%]
TE	Tellurium	[ug/m3@11%]
TL	Thallium	[ug/m3@11%]
SN	Tin	[ug/m3@11%]
TI	Titanium	[ug/m3@11%]
V	Vanadium	[ug/m3@11%]
ZN	Zinc	[ug/m3@11%]
SVOC COMPOUNDS Chlorobenzenes [CB]		
DCB2	1,2-Dichlorobenzene	[ug/m3@11%]
DCB3	1,3-Dichlorobenzene	[ug/m3@11%]
DCB4	1,4-Dichlorobenzene	[ug/m3@11%]
TRICB23	1,2,3-Trichlorobenzene	[ug/m3@11%]
TRICB24	1,2,4-Trichlorobenzene	[ug/m3@11%]
TRICB35	1,3,5-Trichlorobenzene	[ug/m3@11%]
TCB234	1,2,3,4-Tetrachlorobenzene	[ug/m3@11%]
TCB235	1,2,4,5/1,2,3,5-Tetrachlorobenzene	[ug/m3@11%]

PECB	Pentachlorobenzene	[ug/m3@11%]
HXCB	Hexachlorobenzene	[ug/m3@11%]
SVOC COMPOUNDS Chlorophenols [CP]		
DCP23	2,3-Dichlorophenol	[ug/m3@11%]
DCP24	2,4-Dichlorophenol	[ug/m3@11%]
DCP25	2,5-Dichlorophenol	[ug/m3@11%]
DCP26	2,6-Dichlorophenol	[ug/m3@11%]
DCP34	3,4-Dichlorophenol	[ug/m3@11%]
DCP35	3,5-Dichlorophenol	[ug/m3@11%]
TRICP234	2,3,4-Trichlorophenol	[ug/m3@11%]
TRICP235	2,3,5-Trichlorophenol	[ug/m3@11%]
TRICP236	2,3,6-Trichlorophenol	[ug/m3@11%]
TRICP245	2,4,5-Trichlorophenol+	[ug/m3@11%]
TRICP246	2,4,6-Trichlorophenol+	[ug/m3@11%]
TRICP345	3,4,5-Trichlorophenol	[ug/m3@11%]
TCP2345	2,3,4,5-Tetrachlorophenol	[ug/m3@11%]
TCP2346	2,3,4,6-Tetrachlorophenol	[ug/m3@11%]
TCP2356	2,3,5,6-Tetrachlorophenol	[ug/m3@11%]
PECP	Pentachlorophenol TOTAL+	[ug/m3@11%]
SVOC COMPOUNDS Polychlorinatedbiphenyls [PCB]		
MONOCBP	Monochlorobiphenyl	[ng/m3@11%]
DICBP	Dichlorobiphenyl	[ng/m3@11%]
TRICBP	Trichlorobiphenyl	[ng/m3@11%]
TCBP	Tetrachlorobiphenyl	[ng/m3@11%]
PECBP	Pentachlorobiphenyl	[ng/m3@11%]
HXCBP	Hexachlorobiphenyl	[ng/m3@11%]
HPCBP	Heptachlorobiphenyl	[ng/m3@11%]
OCBP	Octachlorobiphenyl	[ng/m3@11%]
NONACBP	Nonachlorobiphenyl	[ng/m3@11%]
DECBP	Decachlorobiphenyl	[ng/m3@11%]
SVOC COMPOUNDS Polyaromatic Hydrocarbons [PAH]		
NAPHELE	Naphthalene+*	[ug/m3@11%]
ACENPHLN	Acenaphthylene	[ug/m3@11%]
ACENATHN	Acenaphthene	[ug/m3@11%]
FLUORENE	Fluorene	[ug/m3@11%]
PHENATHN	Phenanthrene	[ug/m3@11%]
ANTRACNE	Anthracene	[ug/m3@11%]
FLUANTHN	Fluoranthene	[ug/m3@11%]
PYRENE	Pyrene	[ug/m3@11%]
BENZANTH	Benz(a)anthracene	[ug/m3@11%]
CHRYSENE	Chrysene	[ug/m3@11%]
BNZBFLAN	Benzo(b)fluoranthene	[ug/m3@11%]
BNZKFLAN	Benzo(k)fluoranthene	[ug/m3@11%]
BNZCPHEN	Benzo(c)phenanthrene	[ug/m3@11%]
BNZAPYRN	Benzo(a)pyrene	[ug/m3@11%]
INDEPYRN	Indeno(1,2,3-cd)pyrene	[ug/m3@11%]
DIBNZANT	Dibenz(a,h)anthracene	[ug/m3@11%]
BNZPERLN	Benzo(g,h,i)perylene	[ug/m3@11%]
TETRALIN	Tetralin	[ug/m3@11%]
QUINOLN	Quinolin	[ug/m3@11%]
MTLNAPH1	1-Methylnaphthalene	[ug/m3@11%]
MTLNAPH2	2-Methylnaphthalene	[ug/m3@11%]
DMTLNAP3	1,3-Dimethylnaphthalene	[ug/m3@11%]
TMTLNAP5	2,3,5-Trimethylnaphthylene	[ug/m3@11%]
BIPHNYL	Biphenyl	[ug/m3@11%]
CHLNAP2	2-Chloronaphthalene	[ug/m3@11%]
BNZAFLE	Benzo(a)fluorene	[ug/m3@11%]
BNZBFLNE	Benzo(b)fluorene	[ug/m3@11%]
TERPHNLM	m-Terphenyl	[ug/m3@11%]
TERPHNLO	o-Terphenyl	[ug/m3@11%]

Table 1 List of Parameters Recorded for Brookfield Tests

TERPHNLP	p-Terphenyl	[ug/m3@11%]
MTHANCE2	2-Methylanthracene	[ug/m3@11%]
MTHPHN1	1-Methylphenanthrene	[ug/m3@11%]
MTHPHN9	9-Methylphenanthrene	[ug/m3@11%]
DIMTHAN	9,10-Dimethylanthracene	[ug/m3@11%]
BNZEPYRN	Benzo(e)pyrene	[ug/m3@11%]
PERYLENE	Perylene	[ug/m3@11%]
DIMBZAN	7,12-Dimethylbenzo(a)anthracene	[ug/m3@11%]
MTHCLAN	3-Methylcholanthrene	[ug/m3@11%]
CORONENE	Coronene	[ug/m3@11%]
DIBZPYRNh	Dibenzo(a,h)pyrene	[ug/m3@11%]
DIBZPYRNi	Dibenzo(a,i)pyrene	[ug/m3@11%]
DIBZPYRNI	Dibenzo(a,l)pyrene	[ug/m3@11%]
VOLATILE ORGANIC COMPOUNDS by VOST Method		
DCLF12	Dichlorofluoroethane	[ug/m3]
METHCL	Methyl Chloride+	[ug/m3]
VCMONMR	Vinyl Chloride+	[ug/m3]
BROMNMTH	Bromomethane+	[ug/m3]
ETHCL	Ethyl Chloride+ Chloroethane	[ug/m3]
TRICFMN	Trichlorofluoromethane*	[ug/m3]
ACETONE	Acetone* (2-Propanone)	[ug/m3]
DCE11	1,1-Dichloroethylene (ethene)	[ug/m3]
MTHIO	Methyl iodide+ (iodomethane)	[ug/m3]
CS2	Carbon Disulfide+	[ug/m3]
MTHLCL	Methylene Chloride+	[ug/m3]
DICLETN1	1,1-Dichloroethane+	[ug/m3]
DICH12	1,2-Dichloroethene; (trans-1,2-Dichloroethylene)	[ug/m3]
C12DCE	Cis-1,2-Dichloroethene; [dichloroethylene]	[ug/m3]
CLOROFM	Chloroform+	[ug/m3]
DICLETN2	1,2-Dichloroethane+	[ug/m3]
MEK	Methyl Ethyl Ketone+	[ug/m3]
TRICETN	Trichloroethane; [1,1,1-Trichloroethane]	[ug/m3]
CARBET	Carbon Tetrachloride+	[ug/m3]
BENZENE	Benzene+	[ug/m3]
TRICETN2	1,1,2-Trichloroethane+	[ug/m3]
DICLPROP	1,2-Dichloropropane+	[ug/m3]
TRICLETL	Trichloroethene+ [Trichloroethylene]	[ug/m3]
DIBMCBM	Chlorodibromomethane*	[ug/m3]
BMDCMTHN	Bromodichloromethane*	[ug/m3]
C13DCPE	Cis-1,3-Dichloropropene*	[ug/m3]
T13DCPE	Trans-1,3-Dichloropropene*	[ug/m3]
DIBMCBM	Chlorodibromomethane* [Dibromochloromethane]	[ug/m3]
M2P	4-Methyl-2-Pentanone+* [Methyl Isobutyl Ketone MIBK]	[ug/m3]
HX2	2-Hexanone* [MBK]	[ug/m3]
TOLUENE	Toluene+	[ug/m3]
ETLDIBR	Ethylene Dibromide+	[ug/m3]
TETCLETN	Tetrachloroethene+ [Tetrachloroethylene]	[ug/m3]
CB	Chlorobenzene (TOTAL monochlorobenzene)+*	[ug/m3]
TCE1112	1,1,1,2-Tetrachloroethane*	[ug/m3]
ETHBENZ	Ethyl Benzene+	[ug/m3]
XYLENEMP	Sum of m-Xylene and p-Xylene	[ug/m3]
STYRENE	Styrene+	[ug/m3]
XYLENEO	o-Xylene+	[ug/m3]
BROMOFRM	Bromoform+	[ug/m3]
TCE1122	1,1,2,2-Tetrachloroethane+	[ug/m3]
TRICLPRO	1,2,3-Trichloropropane	[ug/m3]
DCB3	1,3-Dichlorobenzene*	[ug/m3]
DCB4	1,4-Dichlorobenzene+*	[ug/m3]
DCB2	1,2-Dichlorobenzene*	[ug/m3]

VOLATILE ORGANICS by Chilled Impinger		
FMLDHYD	Formaldehyde+	[ug/m3]
PHENOL	Phenol+	[ug/m3]
METHANOL	Methanal	[ug/m3]
ACETALD	Acetaldehyde	[ug/m3]
PROPALD	Propionaldehyde	[ug/m3]
ACROLEIN	Acrolein	[ug/m3]
VOLATILE ORGANICS by Tedlar Bag Sample		
DCTFE	1,2-Dichlorotetrafluoroethane [R_114]	[ug/m3]
METHCL	Methyl Chloride+* [Chloromethane]	[ug/m3]
BUTADENE	1,3-Butadiene+	[ug/m3]
ETHANOL	Ethanol [Ethyl Alcohol]	[ug/m3]
TRICFETN	Trichlorotrifluoroethane	[ug/m3]
PROPANL2	2-Propanol*	[ug/m3]
ETHACE	Ethyl Acetate	[ug/m3]
TCE1122	1,1,2,2-Tetrachloroethane	[ug/m3]
ETHT4	4-Ethyltoluene	[ug/m3]
TRIMBZ35	1,3,5-Trimethylbenzene	[ug/m3]
TRIMBZ24	1,2,4-Trimethylbenzene	[ug/m3]
BENZCHLR	Benzyl Chloride+*	[ug/m3]
TRICB24	1,2,4-Trichlorobenzene	[ug/m3]
CUMENE	Cumene, (Isopropylbenzene)	[ug/m3]
DCB2	1,2-Dichlorobenzene*	[ug/m3]
HXCLBUTD	Hexachlorobutadiene+*	[ug/m3]
HEXANEN	N-Hexane+	[ug/m3]
HEPTANE	Heptane	[ug/m3]
CYCHEX	Cyclohexane	[ug/m3]
TETHYFRN	Tetrahydrofuran	[ug/m3]
DXN14	1,4-Dioxane+*	[ug/m3]
VNLBR	Vinyl Bromide+	[ug/m3]
PROPENE	Propene	[ug/m3]
IOSCTANE	Isooctane+ [2,2,4-Trimethylpentane]	[ug/m3]
SVOC COMPOUNDS Dioxins and Furans [PCDD/PCDF]		
TCDF2378	2,3,7,8-Tetrachlorodibenzo-p-furan	[pg TEQ/m3@11%]
TCDD2378	2,3,7,8-Tetrachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
PCDF1	1,2,3,7,8-Pentachlorodibenzo-p-furan	[pg TEQ/m3@11%]
PCDF4	2,3,4,7,8-Pentachlorodibenzo-p-furan	[pg TEQ/m3@11%]
PCDD1	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
HXCDF14	1,2,3,4,7,8-Hexachlorodibenzo-p-furan	[pg TEQ/m3@11%]
HXCDF16	1,2,3,6,7,8-Hexachlorodibenzo-p-furan	[pg TEQ/m3@11%]
HXCDF46	2,3,4,6,7,8-Hexachlorodibenzo-p-furan	[pg TEQ/m3@11%]
HXCDF19	1,2,3,7,8,9-Hexachlorodibenzo-p-furan	[pg TEQ/m3@11%]
HXCDD14	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
HXCDD16	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
HXCDD19	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
HPCDF146	1,2,3,4,6,7,8-Heptachlorodibenzo-p-furan	[pg TEQ/m3@11%]
HPCDF149	1,2,3,4,7,8,9-Heptachlorodibenzo-p-furan	[pg TEQ/m3@11%]
HPCDD146	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
OCDF	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-furan	[pg TEQ/m3@11%]
OCDD	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	[pg TEQ/m3@11%]
TCDF	Total Tetrachlorodibenzofurans	[pg/m3@11%]
PCDF	Total Pentachlorodibenzofurans	[pg/m3@11%]
HXCDF	Total Hexachlorodibenzofurans	[pg/m3@11%]
HPCDF	Total Heptachlorodibenzofurans	[pg/m3@11%]
TCDD	Total Tetrachlorodibenzo-p-dioxins	[pg/m3@11%]
PCDD	Total Pentachlorodibenzo-p-dioxins	[pg/m3@11%]
HXCDD	Total Hexachlorodibenzo-p-dioxins	[pg/m3@11%]
HPCDD	Total Heptachlorodibenzo-p-dioxins	[pg/m3@11%]
KM TEQ _{WHO2005}	TEQ _{WHO2005} Using KM for BDL values	[pg TEQ/m3@11%]

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	TSP	CO	NOX	SOX	HF	PM10	PM2.5	NH4	CL2	HCl	THC	HG	AL	SB	AS	
			[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3@11%]	[mg/m3]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	
43040	Blank	17B									0.01	0.70	0.12		0.01		-0.68	-0.18
43040	Test 1	17B	34.35	214.18	988.14	581.45	0.41	19.40	13.70	9.94	3.45	32.14	8.08	3.50			-0.70	0.89
43040	Test 2	17B	26.43	216.33	998.69	625.18	0.37	14.40	10.60	11.46	4.58	34.99	16.20	3.83			-0.67	0.38
43040	Test 3	17B	29.37	219.90	917.81	783.90	0.14	21.40	13.20	7.86	1.12	7.30	15.30	4.15			-0.66	0.34
43665	Blank	19B									0.02	-0.58	0.53		0.10	55.95	1.17	0.66
43665	Test 1	19B	47.17	294.83	602.53	576.23	0.25	29.10	15.20	5.29	-0.58	9.14	8.15	4.03	450.71	1.98	1.73	
43665	Test 2	19B	31.21	312.69	621.27	751.71	0.10	17.30	7.75	5.86	-0.59	9.28	7.57	3.92	333.02	2.03	1.78	
43665	Test 3	19B	53.49	304.48	565.16	540.37	0.11	40.80	14.70	6.37	-0.59	7.35	7.82	4.01	544.36	2.04	2.00	
43739	Blank	19TB													0.11	87.25	2.41	0.72
43739	Test 1	19TB	49.76	256.92	754.05	400.84	0.21	30.30	12.60				6.38	5.97	828.68	2.40	1.17	
43739	Test 2	19TB	93.77	255.38	738.65	421.67	0.13	59.00	23.80				6.80	6.44	721.44	2.47	1.09	
43739	Test 3	19TB	92.12	252.59	845.34	353.98	0.08						6.67					
44105	Blank	20TB					-0.04			-0.06	-0.05	-0.06		0.37	127.09	0.15	0.66	
44105	Test 1	20TB	28.32				0.11	27.90	16.3	0.64	0.13	7.77		2.01	444.68	0.13	0.58	
44105	Test 2	20TB	40.37				-0.10	26.80	10.8	6.97	-0.08	8.19		1.27	574.20	0.16	0.75	
44105	Test 3	20TB	46.22				0.21	31.50	14.2	9.91	-0.07	7.19		2.22	597.69	0.27	0.88	

TESTDATE	SAMPLEID	SERIES	BA	BE	B	BI	CD	CA	CR	COB	CU	FE	PB	LI	MG	MN	MO	
			[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	
43040	Blank	17B	4.50	-0.04	-6.75	-0.14	-0.04			-0.68	-0.04	0.43	8.01	0.14	0.68		3.35	2.61
43040	Test 1	17B	21.34	-0.04	118.39	0.48	0.25			4.11	0.29	3.11	146.88	25.45	4.86		14.50	3.13
43040	Test 2	17B	22.22	-0.04	34.29	0.25	0.20			2.25	0.20	1.91	144.51	28.28	6.75		10.02	2.98
43040	Test 3	17B	21.77	-0.04	76.38	0.15	0.15			11.37	0.15	1.84	158.46	28.09	6.32		8.67	4.35
43665	Blank	19B	5.13	0.16	15.24	0.40	0.16	83.24		1.66	0.16	1.16	21.27	0.61	2.81	20.31	1.81	4.67
43647	Test 1	19B	26.94	0.34	51.84	1.01	0.44	5513.13		8.32	0.40	3.32	340.55	36.57	9.52	164.35	13.57	6.13
43647	Test 2	19B	22.75	0.35	58.64	1.04	0.52	3999.56		21.21	0.49	8.25	415.47	21.47	5.79	127.47	12.91	8.09
43647	Test 3	19B	30.15	0.35	68.40	1.04	0.53	6916.21		10.96	0.48	4.02	377.70	38.77	9.59	203.03	16.88	7.27
43739	Blank	19TB	7.52	0.16	26.95	0.54	0.16	103.70		2.70	0.16	18.69	18.94	0.76	3.08	22.05	1.37	5.34
43739	Test 1	19TB	22.07	0.19	30.77	0.61	0.23	10795.91		5.24	0.32	2.43	542.26	23.90	7.79	245.72	19.38	5.87
43739	Test 2	19TB	24.06	0.19	31.59	0.63	0.25	12034.25		3.87	0.29	2.29	346.38	28.49	9.03	252.96	19.32	5.75
43739	Test 3	19TB																
44105	Blank	20TB	6.19	0.15	108.27	0.33	0.07	427.71		1.11	0.15	2.18	127.12	0.35	0.44	145.27	0.87	6.31
44105	Test 1	20TB	10.37	0.13	104.45	0.29	0.22	5923.27		3.18	0.30	3.00	271.51	20.31	3.70	253.25	13.76	5.82
44105	Test 2	20TB	12.65	0.16	123.42	0.35	0.14	8074.05		4.79	0.37	3.21	424.30	21.88	4.92	323.75	31.39	7.19
44105	Test 3	20TB	14.39	0.16	148.19	0.36	0.34	8619.57		7.89	0.49	7.78	541.11	31.52	6.09	355.59	17.21	8.05

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	NI	P	SE	SI	AG	NA	SR	TL	TE	SN	TI	V	ZN
			[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]
43040	Blank	17B	1.31	-20.26	-0.45		-0.05		-20.48	0.06	-0.45	20.03	2.66	-0.14	-2.25
43040	Test 1	17B	9.60	-21.02	1.66		2.10		3.32	18.10	-0.47	36.20	8.31	4.72	25.92
43040	Test 2	17B	7.28	-20.04	-20.04		1.78		1.86	4.79	-0.58	29.61	9.28	2.74	-11.13
43040	Test 3	17B	5.57	-19.75	4.72		1.62		4.04	31.82	-0.44	41.26	8.52	2.37	-10.97
43665	Blank	19B	1.42	59.79	1.64	76.91	0.27	152.65	0.60	0.55	0.82	7.36	7.74	0.49	8.77
43647	Test 1	19B	4.63	152.07	4.45	432.95	0.84	324.88	8.39	36.75	0.81	54.91	19.03	2.47	66.82
43647	Test 2	19B	13.36	156.06	3.95	567.95	2.77	328.67	6.64	28.92	0.83	35.92	15.49	2.12	25.77
43647	Test 3	19B	9.16	156.21	5.07	571.12	1.20	300.59	10.56	31.76	0.83	46.37	20.05	5.66	36.92
43739	Blank	19TB	1.45	84.19	1.80	78.80	0.22	269.52	1.01	0.22	0.90	17.89	19.48	0.54	10.37
43739	Test 1	19TB	4.64	91.35	2.55	438.94	0.50	286.06	16.97	30.35	0.84	10.91	41.44	2.42	16.11
43739	Test 2	19TB	3.70	93.77	2.47	4138.25	0.31	223.82	18.26	33.92	0.93	6.96	35.71	2.18	13.08
43739	Test 3	19TB													
44105	Blank	20TB	0.60	67.30	1.50	97.51	0.15	931.39	0.73	0.16	1.12	17.47	6.28	0.63	6.85
44105	Test 1	20TB	3.36	59.11	1.77	882.70	0.17	1227.11	8.11	22.04	0.99	22.34	11.91	2.38	9.43
44105	Test 2	20TB	3.84	70.70	1.79	426.37	0.24	1571.32	11.37	21.57	1.18	26.36	17.01	2.64	11.88
44105	Test 3	20TB	6.63	74.01	1.66	316.77	0.45	1907.86	11.92	28.36	1.23	33.51	19.78	3.06	19.37

TESTDATE	SAMPLEID	SERIES	DCB2	DCB3	DCB4	TRICB23	TRICB24	TRICB35	TCB234	TCB235	PECB	HXCB	DCP23	DCP24	DCP25	DCP26	DCP34	
			[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	
43040	Blank	17B	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	0.00	-0.07	-0.07	-0.07
43040	Test 1	17B	0.17	0.41	0.52	-0.07	0.11	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	0.00	-0.55	0.07	0.07
43040	Test 2	17B																
43040	Test 3	17B	-12.56	0.26	0.39	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	0.00	-0.34	-0.07	-0.07
43665	Blank	19B	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48	-0.48
43647	Test 1	19B	-0.44	0.47	0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44	-0.44
43647	Test 2	19B	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64	-50.64
43647	Test 3	19B	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51	-0.51
43739	Blank	19TB																
43739	Test 1	19TB																
43739	Test 2	19TB																
43739	Test 3	19TB																
44105	Blank	20TB	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44105	Test 1	20TB	0.47	0.51	0.60	0.01	0.07	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44105	Test 2	20TB	0.35	0.46	0.51	0.01	0.07	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44105	Test 3	20TB	0.26	0.37	0.42	0.01	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	DCP35 [ug/m3@11%]	TRICP234 [ug/m3@11%]	TRICP235 [ug/m3@11%]	TRICP236 [ug/m3@11%]	TRICP245 [ug/m3@11%]	TRICP246 [ug/m3@11%]	TRICP345 [ug/m3@11%]	TCP2345 [ug/m3@11%]	TCP2346 [ug/m3@11%]	TCP2356 [ug/m3@11%]	PECP [ug/m3@11%]	MONOCBP [ng/m3@11%]	DICBP [ng/m3@11%]	TRICBP [ng/m3@11%]	TCBP [ng/m3@11%]
43040	Blank	17B	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.01	0.07	0.174	0.406
43040	Test 1	17B	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	357.54	47.53	5.276	2.115
43040	Test 2	17B															
43040	Test 3	17B	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	-0.07	237.54	34.49	5.345	54.589
43665	Blank	19B														0.418	0.293
43647	Test 1	19B														2.009	1.322
43647	Test 2	19B														7.951	5.966
43647	Test 3	19B														1.932	1.421
43739	Blank	19TB															
43739	Test 1	19TB															
43739	Test 2	19TB															
43739	Test 3	19TB															
44105	Blank	20TB												3.76	0.17	0.105	0.163
44105	Test 1	20TB												240.02	20.16	2.711	0.991
44105	Test 2	20TB												245.50	19.10	2.477	0.820
44105	Test 3	20TB												212.79	16.97	2.455	1.449

TESTDATE	SAMPLEID	SERIES	PECBP [ng/m3@11%]	HXCBP [ng/m3@11%]	HPCBP [ng/m3@11%]	OCBP [ng/m3@11%]	NONACBP [ng/m3@11%]	DECBP [ng/m3@11%]	NAPHLENE [ug/m3@11%]	ACENPHLN [ug/m3@11%]	ACENATHN [ug/m3@11%]	FLUORENE [ug/m3@11%]	PHENATHN [ug/m3@11%]	ANTRACNE [ug/m3@11%]	FLUANATHN [ug/m3@11%]	PYRENE [ug/m3@11%]	BENZANTH [ug/m3@11%]
43040	Blank	17B	0.337	0.186	-0.021	-0.010	-0.010	-0.008	-0.134	-0.067	-0.067	-0.067	-0.067	-0.067	-0.067	-0.067	-0.067
43040	Test 1	17B	1.251	0.682	0.211	-0.033	-0.017	-0.031	104.646	3.597	1.334	1.772	12.121	0.595	1.493	0.647	0.266
43040	Test 2	17B															
43040	Test 3	17B	3.860	1.487	0.148	-0.025	-0.023	-0.027	52.990	1.935	0.256	1.131	8.337	0.356	1.108	0.521	0.164
43665	Blank	19B	0.264	0.068	0.007	-0.003	-0.002	0.001	1.258	-0.002	5.228	0.026	0.059	-0.002	0.007	0.004	-0.002
43647	Test 1	19B	1.691	0.618	0.065	0.007	0.003	0.006	57.135	2.408	0.306	1.635	11.673	0.865	1.160	0.596	0.139
43647	Test 2	19B	4.033	1.070	0.133	0.013	0.004	-0.004	59.558	2.066	0.259	1.633	11.243	0.812	0.978	0.515	0.121
43647	Test 3	19B	1.073	0.341	0.029	0.007	-0.005	0.006	50.967	1.626	0.254	1.320	9.808	0.463	0.914	0.495	0.131
43739	Blank	19TB															
43739	Test 1	19TB															
43739	Test 2	19TB															
43739	Test 3	19TB															
44105	Blank	20TB	0.095	0.038	0.003	-0.001	0.010	0.045	0.029	0.005	0.044	0.392	0.014	0.006	0.003	0.007	-0.002
44105	Test 1	20TB	0.544	0.214	0.046	0.013	0.018	0.069	152.015	3.311	0.128	1.916	7.801	0.378	0.982	0.598	0.200
44105	Test 2	20TB	0.527	0.198	0.042	0.012	0.012	0.057	172.297	3.176	0.203	1.466	8.536	0.444	0.964	0.577	0.216
44105	Test 3	20TB	0.621	0.240	0.048	0.011	0.017	0.059	183.908	3.490	0.130	1.601	8.955	0.426	0.997	0.578	0.200

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	CHRYSENE	BNZBFLAN	BNZKFLAN	BNZCPHEN	BNZAPYRN	INDEPYRN	DIBNZANT	BNZPERLN	MTLNAPH1	MTLNAPH2	DMTLNAP3	TMTLNAP5	BIPHNYL	CHLNAP2	BNZAFLE
			[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]
43040	Blank	17B	-0.067	-0.067	-0.067		-0.067	-0.067	-0.067	-0.067				-0.067			
43040	Test 1	17B	2.464	0.458	-0.065		-0.065	-0.065	-0.065	0.155				23.545			
43040	Test 2	17B															
43040	Test 3	17B	1.907	0.336	-0.069		-0.069	-0.069	-0.069	0.126				14.481			
43665	Blank	19B	-0.002	0.008	0.000	-0.002	-0.001	0.001	-0.002	-0.002	0.008	0.014	0.155	0.012			
43647	Test 1	19B	2.567	0.415	0.091	-0.018	0.086	0.031	0.053	0.106	8.772	13.414	13.959	1.129			
43647	Test 2	19B	2.492	0.348	0.106	0.316	0.110	0.031	0.062	0.062	9.319	2.998	11.750	1.165			
43647	Test 3	19B	2.335	0.339	0.037	-0.020	0.064	0.032	0.034	0.120	7.940	12.387	8.752	1.082			
43739	Blank	19TB															
43739	Test 1	19TB															
43739	Test 2	19TB															
43739	Test 3	19TB															
44105	Blank	20TB	-0.002	-0.002	-0.002		0.004	-0.002	-0.002	0.007	0.006	0.004					
44105	Test 1	20TB	2.534	0.338	0.055		0.025	0.015	0.044	0.096	13.624	11.646					
44105	Test 2	20TB	2.568	0.367	0.052		0.039	0.017	0.047	0.103	14.910	13.086					
44105	Test 3	20TB	2.431	0.351	0.136		0.034	0.015	0.045	0.093	16.080	13.913					
TESTDATE	SAMPLEID	SERIES	BNZBFLNE	TERPHNLM	TERPHNLO	TERPHNLP	MTHANCE2	MTHPHN1	MTHPHN9	DIMTHAN	BNZEPYRN	PERYLENE	DIMBZAN	MTHCLAN	CORONENE	DIBZPYRN	DIBZPYRNh
			[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]	[ug/m3@11%]
43040	Blank	17B									-0.067	-0.268					
43040	Test 1	17B									0.604	-0.262					
43040	Test 2	17B															
43040	Test 3	17B									0.523	-0.274					
43665	Blank	19B									-0.001	0.000	-0.002	-0.010			-0.010
43647	Test 1	19B									0.673	-0.008	-0.018	-0.088			-0.088
43647	Test 2	19B									0.739	-0.022	-0.020	-0.101			-0.101
43647	Test 3	19B									0.701	0.014	0.041	-0.102			-0.102
43739	Blank	19TB															
43739	Test 1	19TB															
43739	Test 2	19TB															
43739	Test 3	19TB															
44105	Blank	20TB									0.003	-0.002					
44105	Test 1	20TB									0.805	0.005					
44105	Test 2	20TB									0.518	0.005					
44105	Test 3	20TB									0.503	0.008					

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	DIBZPYRNI [ug/m3@11%]	DIBZPYRNI [ug/m3@11%]	METHCL [ug/m3]	VCMONMR [ug/m3]	BROMNMT [ug/m3]	ETHCL [ug/m3]	TRICFMN [ug/m3]	ACETONE [ug/m3]	DCE11 [ug/m3]	MTHIO [ug/m3]	CS2 [ug/m3]	METHCL [ug/m3]	DICLETN1 [ug/m3]	DICH12 [ug/m3]
43040	Blank	17B			-0.722	-0.626	-0.722	-0.433	-0.482	-2.17	-0.53	-0.72	-1.25	-0.91	-0.58	-0.48
43040	Test 1	17B			415.865	35.721	10.673	6.106	-0.481	57.69	-0.53	16.63	411.54	-0.91	-0.58	-0.48
43040	Test 2	17B			408.173	47.115	-36.058	-21.635	-24.038	-110.58	-26.44	-36.06	1052.88	-45.67	-28.85	-24.04
43040	Test 3	17B			132.850	38.647	-36.232	-21.739	-24.155	-111.11	-26.57	-36.23	565.22	-45.89	-28.99	-24.15
43665	Blank	19B	-0.010	-0.002	2.714	-0.641	-0.740	-0.444	-0.493	-2.22	-0.54	-0.74	-1.28	-0.94	-0.59	-0.49
43647	Test 1	19B	-0.088	0.076	358.911	40.000	14.703	6.040	-0.495	93.56	-0.54	9.60	310.89	-1.98	-0.59	-0.50
43647	Test 2	19B	-0.101	0.088	334.483	46.305	22.167	-8.867	-9.852	83.74	-10.84	-14.78	387.19	-18.72	-11.82	-9.85
43647	Test 3	19B	-0.102	0.435	551.724	32.020	27.094	-8.867	-9.852	70.44	-10.84	17.24	397.54	-18.72	-11.82	-9.85
43739	Blank	19TB			3.941	-0.640	-0.739	-0.443	-0.493	-2.22	-0.54	-0.74	-1.28	-0.94	-0.59	-0.49
43739	Test 1	19TB			298.000	23.400	7.300	2.950	-0.500	70.50	-0.55	3.65	299.00	-0.95	-0.60	-0.50
43739	Test 2	19TB			2525.000	-26.000	100.500	-18.900	-20.000	-90.00	-22.00	-30.00	315.00	-38.00	-24.00	-20.00
43739	Test 3	19TB			4009.569	-24.880	76.077	-17.225	-19.139	-86.12	-21.05	67.46	349.28	-36.36	-22.97	-19.14
44105	Blank	20TB														
44105	Test 1	20TB														
44105	Test 2	20TB														
44105	Test 3	20TB														

TESTDATE	SAMPLEID	SERIES	C12DCE [ug/m3]	CLOROFM [ug/m3]	DICLETN2 [ug/m3]	MEK [ug/m3]	TRICETN [ug/m3]	CARBET [ug/m3]	BENZENE [ug/m3]	TRICETN2 [ug/m3]	DICLPROP [ug/m3]	TRICLETL [ug/m3]	DIBMCBM [ug/m3]	BMDCMTHN [ug/m3]	C13DCPE [ug/m3]	T13DCPE [ug/m3]	DIBMCBM [ug/m3]
43040	Blank	17B	-0.48	-0.53	-0.34	-1.73	-0.67	-0.77	-0.43	-0.77	-0.53	-0.53	-0.48	-0.53	-0.48	-0.34	-0.43
43040	Test 1	17B	-0.48	-0.53	-0.34	12.31	-0.67	-0.77	470.67	-0.77	-0.53	-0.53	-0.48	-0.53	-0.48	-0.34	-0.43
43040	Test 2	17B	-24.04	-26.44	-16.83	-86.54	-33.65	-38.46	2115.38	-38.46	-26.44	-26.44	-24.04	-26.44	-24.04	-16.83	-21.63
43040	Test 3	17B	-24.15	-26.57	-16.91	-86.96	-33.82	-38.65	1550.72	-38.65	-26.57	-26.57	-24.15	-26.57	-24.15	-16.91	-21.74
43665	Blank	19B	-0.49	-0.54	-0.35	-1.78	-0.69	-0.79	1.85	-0.79	-0.54	-0.54	-0.49	-0.54	-0.49	-0.35	-0.44
43647	Test 1	19B	-0.50	-0.54	-0.35	29.55	-0.69	-0.79	354.95	-0.79	-0.54	-0.54	-0.50	-0.54	-0.50	-0.35	-0.45
43647	Test 2	19B	-9.85	-10.84	-6.90	-35.47	-13.79	-15.76	1546.80	-15.76	-10.84	-10.84	-9.85	-0.54	-9.85	-6.90	-8.87
43647	Test 3	19B	-9.85	-10.84	-6.90	-35.47	-13.79	-15.76	1364.53	-15.76	-10.84	-10.84	-9.85	-0.54	-9.85	-6.90	-8.87
43739	Blank	19TB	-0.49	-0.54	-0.34	-1.77	-0.69	-0.79	-0.44	-0.79	-0.54	-0.54	0.00	-0.54	-0.49	-0.34	-0.44
43739	Test 1	19TB	-0.50	-0.55	-0.35	11.85	-0.70	-0.80	428.50	-0.80	-0.55	-0.55	0.00	-0.55	-0.50	-0.35	-0.45
43739	Test 2	19TB	-20.00	-22.00	-14.00	-70.00	-28.00	-32.00	975.00	-32.00	-22.00	-22.00	0.00	-22.00	-20.00	-14.00	-18.00
43739	Test 3	19TB	-19.14	-21.05	-13.40	-66.99	-26.79	-30.62	1071.77	-30.62	-21.05	-21.05	0.00	-21.05	-19.14	-13.40	-17.22
44105	Blank	20TB															
44105	Test 1	20TB															
44105	Test 2	20TB															
44105	Test 3	20TB															

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	M2P [ug/m3]	HX2 [ug/m3]	TOLUENE [ug/m3]	ETLDIBR [ug/m3]	TETCLETN [ug/m3]	CB [ug/m3]	TCE1112 [ug/m3]	ETHBENZ [ug/m3]	XYLENEMP [ug/m3]	STYRENE [ug/m3]	XYLENEO [ug/m3]	BROMOFRM [ug/m3]	TCE1122 [ug/m3]	TRICLPRO [ug/m3]	DCB3 [ug/m3]
43040	Blank	17B	-0.91	-1.49	-0.67	-0.48	-0.87	-0.53	-0.48	-0.67	-0.72	-0.58	-0.72	-0.67	-0.67	-0.72	-0.96
43040	Test 1	17B	-2.12	3.99	166.35	-0.48	-0.87	17.12	-0.48	44.47	92.31	40.63	42.93	-0.67	-0.67	-0.72	1.15
43040	Test 2	17B	-45.67	-76.92	504.81	-24.04	-43.27	-26.44	-24.04	73.56	132.21	45.19	59.13	-33.65	-33.65	-36.06	-48.08
43040	Test 3	17B	-45.89	-77.29	372.95	-24.15	-43.48	-26.57	-24.15	49.28	108.70	31.40	48.31	-33.82	-33.82	-36.23	-48.31
43665	Blank	19B	-0.94	-1.53	-0.69	-0.49	-0.89	-0.54	-0.49	-0.69	-0.74	-0.59	-0.74	-0.69	0	-0.74	-0.99
43647	Test 1	19B	2.18	9.06	107.43	-0.50	-0.89	17.67	-0.50	36.34	66.83	41.34	29.31	-0.69	0	-0.74	-0.99
43647	Test 2	19B	-18.72	-30.54	290.15	-9.85	-17.73	19.70	-9.85	40.89	85.22	75.37	36.45	-13.79	0	-14.78	-19.70
43647	Test 3	19B	-18.72	-30.54	245.81	-9.85	-17.73	16.75	-9.85	34.48	74.38	64.04	31.03	-11.82	0	-14.78	-19.70
43739	Blank	19TB	-0.94	-1.53	2.96	-0.49	-0.89	-0.54	-0.49	-0.69	-0.74	-0.59	-0.74	-0.69	0	-0.74	-0.99
43739	Test 1	19TB	-0.95	2.25	140.50	-0.50	-0.90	12.40	-0.50	25.70	54.50	45.40	23.05	-0.70	0	-0.75	-1.00
43739	Test 2	19TB	-38.00	-60.00	225.00	-20.00	-36.00	-22.00	-20.00	-28.00	57.00	24.00	-30.00	-28.00	0	-30.00	-40.00
43739	Test 3	19TB	-36.36	-57.42	222.97	-19.14	-34.45	-21.05	-19.14	27.75	63.16	31.10	-28.71	-26.79	0	-28.71	-38.28
44105	Blank	20TB															
44105	Test 1	20TB															
44105	Test 2	20TB															
44105	Test 3	20TB															

TESTDATE	SAMPLEID	SERIES	DCB4 [ug/m3]	DCB2 [ug/m3]	FMLDHYD [ug/m3]	PHENOL [ug/m3]	METHANOL [ug/m3]	ACETALD [ug/m3]	PROPALD [ug/m3]	ACROLEIN [ug/m3]	DCTFE [ug/m3]	METHCL [ug/m3]	BUTADENE [ug/m3]	ETHANOL [ug/m3]	TRICFETN [ug/m3]	PROPANL2 [ug/m3]	ETHACE [ug/m3]
43040	Blank	17B	-0.96	-0.96	-200.82	-2008.20											
43040	Test 1	17B	1.11	-0.96	-142.34	-1423.36					-4.61	-2.41	-32.23	21.55	-4.47	-9.54	-13.98
43040	Test 2	17B	-48.08	-48.08	-158.60	-1586.02					-4.61	-2.41	-32.23	-7.32	-4.47	-9.54	-13.98
43040	Test 3	17B	-48.31	-48.31	-180.95	-1809.52					-4.61	-2.41	-30.10	-7.32	-4.47	-9.54	-13.98
43665	Blank	19B	-0.99	-0.99	67.64	-676.44	-338.22	101.47	54.11	-3.38			-498.42				
43647	Test 1	19B	-0.99	-0.99	752.41	-643.09	-321.54	893.89	530.55	-3.22	-13.10	115.00	618.45	36.60	-12.60	338.00	-39.60
43647	Test 2	19B	-19.70	-19.70	3104.73	-675.68	-337.84	3479.73	212.84	1631.76	-13.10	114.00	549.07	23.50	-12.60	35.00	-39.60
43647	Test 3	19B	-19.70	-19.70	403.57	-714.29	-357.14	2692.86	210.71	875.00	-12.70	155.00	-497.36	-20.20	-12.30	-26.30	-38.60
43739	Blank	19TB	-0.99	-0.99	61.49			-3.38	-3.38	-3.38							
43739	Test 1	19TB	-1.00	-1.00	138.93			1976.51	136.91	882.55	-1.19	82.10	239.40	16.20	-1.15	-2.46	13.10
43739	Test 2	19TB	-40.00	-40.00	11885.52			2178.45	170.54	199.83			409.30				
43739	Test 3	19TB	-38.28	-38.28	2382.25			1744.03	129.01	698.29	-1.19	79.00	-99.47	15.20	-1.15	-2.46	12.60
44105	Blank	20TB															
44105	Test 1	20TB															
44105	Test 2	20TB															
44105	Test 3	20TB															

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	TCE1122 [ug/m3]	ETHHT4 [ug/m3]	TRIMBZ35 [ug/m3]	TRIMBZ24 [ug/m3]	BENZCHLR [ug/m3]	TRICB24 [ug/m3]	CUMENE [ug/m3]	DCB2 [ug/m3]	HXCLBUTD [ug/m3]	HEXANEN [ug/m3]
43040	Blank	17B										
43040	Test 1	17B		-9.54	-9.53	-9.53	-10.10			-5.83	-20.68	41.07
43040	Test 2	17B		-9.54	-9.53	-9.53	-10.10			-2.33	-20.68	42.72
43040	Test 3	17B		-9.54	-9.53	-9.53	-10.10			-2.33	-20.68	36.02
43665	Blank	19B										
43647	Test 1	19B	-7.55	-27.00	-27.00	-27.00	-28.50	-40.80	-27.00		-58.70	46.90
43647	Test 2	19B	-7.55	-27.00	-27.00	-27.00	-28.50	-40.80	-27.00		-58.70	52.60
43647	Test 3	19B	-7.35	-26.30	-26.30	-26.30	-27.70	-39.70	-26.30		-57.10	54.90
43739	Blank	19TB										
43739	Test 1	19TB	-0.69	-2.46	-2.45	4.91	-2.59	-3.71	-2.46		-5.33	75.10
43739	Test 2	19TB										
43739	Test 3	19TB	-0.69	-2.46	-2.45	5.28	-2.59	-3.71	-2.46		-5.33	84.80
44105	Blank	20TB										
44105	Test 1	20TB										
44105	Test 2	20TB										
44105	Test 3	20TB										

TESTDATE	SAMPLEID	SERIES	HEPTANE [ug/m3]	CYCHEX [ug/m3]	TETHYFRN [ug/m3]	DXN14 [ug/m3]	VNLBR [ug/m3]	PROPENE [ug/m3]	IOSCTANE [ug/m3]
43040	Blank	17B							
43040	Test 1	17B	33.98	-2.67	-12.91	-13.98	-3.40	1844.66	-3.63
43040	Test 2	17B	36.60	-2.67	329.13	-13.98	-3.40	1825.24	-3.63
43040	Test 3	17B	34.08	-2.67	1757.28	-13.98	-3.40	1766.99	-3.63
43665	Blank	19B							
43647	Test 1	19B	24.00	-9.64	18.00	-39.60	-9.62	1310.00	-10.30
43647	Test 2	19B	24.60	-9.64	22.10	-39.60	-9.62	1390.00	-10.30
43647	Test 3	19B	31.40	8.94	-28.00	-38.60	-9.36	1600.00	-10.00
43739	Blank	19TB							
43739	Test 1	19TB	28.70	9.29	4.17	-3.60	4.66	1380.00	-0.93
43739	Test 2	19TB							
43739	Test 3	19TB	29.80	9.54	5.57	5.72	4.51	1350.00	-0.93
44105	Blank	20TB							
44105	Test 1	20TB							
44105	Test 2	20TB							
44105	Test 3	20TB							

Table 2 Brookfield Test Results

TESTDATE	SAMPLEID	SERIES	TCDF2378 <small>[pg TEQ/m3@11]</small>	TCDD2378 <small>[pg TEQ/m3@11]</small>	PCDF1 <small>[pg TEQ/m3@11]</small>	PCDF4 <small>[pg TEQ/m3@11]</small>	PCDD1 <small>[pg TEQ/m3@11]</small>	HXCDF14 <small>[pg TEQ/m3@11]</small>	HXCDF16 <small>[pg TEQ/m3@11]</small>	HXCDF46 <small>[pg TEQ/m3@11]</small>	HXCDF19 <small>[pg TEQ/m3@11]</small>	HXCDD14 <small>[pg TEQ/m3@11]</small>	HXCDD16 <small>[pg TEQ/m3@11]</small>	HXCDD19 <small>[pg TEQ/m3@11%]</small>	HPCDF146 <small>[pg TEQ/m3@11]</small>	HPCDF149 <small>[pg TEQ/m3@11%]</small>
43040	Blank	17B	-0.156	-1.473	-0.076	-0.736	-0.770	-0.158	-0.152	-0.170	-0.174	-0.183	-0.165	-0.158	-0.012	-0.015
43040	Test 1	17B	30.522	5.603	1.055	17.877	3.586	2.355	1.203	1.391	0.358	0.307	0.323	0.624	0.217	0.112
43040	Test 2	17B														
43040	Test 3	17B	23.526	4.385	0.584	8.325	1.028	0.564	0.299	0.308	-0.180	-0.162	-0.146	-0.139	0.034	-0.016
43665	Blank	19B	0.039	-0.367	-0.024	-0.106	-0.116	-0.023	-0.014	-0.015	0.058	-0.019	0.026	-0.019	-0.003	-0.002
43647	Test 1	19B	5.643	1.793	0.328	3.736	-0.360	0.207	-0.132	-0.127	-0.037	0.034	0.049	-0.025	0.024	-0.003
43647	Test 2	19B	9.157	3.890	0.681	7.890	1.347	0.446	0.438	0.494	0.338	0.082	0.091	0.124	0.076	0.014
43647	Test 3	19B	7.290	2.559	0.384	4.467	0.685	0.183	0.172	0.186	0.116	0.061	-0.071	-0.055	0.031	0.009
43739	Blank	19TB														
43739	Test 1	19TB														
43739	Test 2	19TB														
43739	Test 3	19TB														
44105	Blank	20TB	-0.119	-1.512	-0.027	-0.254	-0.985	-0.064	-0.062	-0.069	-0.078	-0.131	-0.117	-0.126	-0.010	-0.012
44105	Test 1	20TB	6.912	-1.311	0.215	-2.467	-1.311	-0.129	-0.084	-0.093	-0.107	-0.102	-0.089	-0.098	-0.024	-0.011
44105	Test 2	20TB	5.991	-2.928	0.176	1.885	-1.644	-0.101	0.191	-0.135	-0.124	-0.119	-0.104	-0.115	0.047	-0.012
44105	Test 3	20TB	3.563	-1.781	-0.123	-1.011	-1.372	0.202	0.231	-0.113	-0.130	-0.185	-0.164	-0.178	-0.026	-0.020

TESTDATE	SAMPLEID	SERIES	HPCDD146 <small>[pg TEQ/m3@11]</small>	OCDF <small>[pg TEQ/m3@11]</small>	OCDD <small>[pg TEQ/m3@11]</small>	TCDF <small>[pg/m3@11%]</small>	PCDF <small>[pg/m3@11%]</small>	HXCDF <small>[pg/m3@11%]</small>	HPCDF <small>[pg/m3@11%]</small>	TCDD <small>[pg/m3@11%]</small>	PCDD <small>[pg/m3@11%]</small>	HXCDD <small>[pg/m3@11%]</small>	HPCDD <small>[pg/m3@11%]</small>	KM TEQwho <small>[pg TEQ/m3@11%]</small>
43040	Blank	17B	-0.016	0.002	0.009	-1.562	-1.495	-1.629	-1.361	-1.473	-1.539	-1.673	-1.562	0.099
43040	Test 1	17B	0.078	0.073	0.028	1504.281	361.899	103.556	51.233	147.812	102.902	40.986	14.498	65.711
43040	Test 2	17B												
43040	Test 3	17B	0.022	0.002	0.005	1247.093	143.895	20.328	3.380	54.817	17.861	2.467	2.193	39.137
43665	Blank	19B	0.007	0.001	0.004	0.394	-0.231	0.577	-0.149	-0.367	-0.231	0.260	0.712	0.185
43647	Test 1	19B	0.018	0.001	0.005	740.118	78.583	5.503	2.356	25.843	4.290	1.566	1.846	11.954
43647	Test 2	19B	0.038	0.003	0.010	1300.555	181.308	37.274	11.425	87.514	13.674	16.895	7.394	25.118
43647	Test 3	19B	0.037	0.002	0.007	915.791	99.904	11.534	4.650	237.578	84.675	29.037	6.234	16.229
43739	Blank	19TB												
43739	Test 1	19TB												
43739	Test 2	19TB												
43739	Test 3	19TB												
44105	Blank	20TB	-0.016	0.001	0.004	-1.192	1.501	-0.779	-1.237	-1.512	-0.985	-1.306	-1.581	0.045
44105	Test 1	20TB	0.039	-0.002	-0.004	875.640	56.672	-1.067	-1.133	18.091	7.712	-1.022	8.956	7.292
44105	Test 2	20TB	0.048	-0.002	0.008	648.649	26.126	5.698	4.707	15.631	-1.644	-1.194	4.797	8.695
44105	Test 3	20TB	-0.039	-0.003	0.006	479.027	27.923	10.110	-2.022	15.045	-1.372	5.392	-3.370	4.136

Independent Samples Test comparison of Baseline 2017 and Baseline 2019

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper	
1	LnCO	Equal variances assumed	1.173	.340	-18.112	4	.0001	-.3378	.0187	-.3896	-.2860
2	LnNOx	Equal variances assumed	.000	.996	12.587	4	.0002	.4847	.0385	.3778	.5917
3	LnNH4	Equal variances assumed	1.405	.302	4.112	4	.0147	.5037	.1225	.1636	.8437
4	LnAs	Equal variances not assumed	10.578	.031	-4.295	2.085	.0466	-1.32769	.30913	-2.60739	-.04799
5	LnCd	Equal variances assumed	1.495	.289	-5.685	4	.0047	-.9291	.1634	-1.3829	-.4753
6	LnCob	Equal variances assumed	2.284	.205	-3.886	4	.0177	-.7894	.2031	-1.3533	-.2255
7	LnFe	Equal variances assumed	.775	.428	-14.391	4	.0001	-.9219	.0641	-1.0997	-.7440
8	LnMo	Equal variances assumed	.992	.376	-5.085	4	.0071	-.7278	.1431	-1.1252	-.3304
9	LnSr	Equal variances assumed	1.429	.298	-3.934	4	.0170	-1.0533	.2677	-1.7967	-.3100
10	LnTi	Equal variances assumed	3.331	.142	-8.547	4	.0010	-.7320	.0857	-.9698	-.4942
11	LnBNZEPYRN	Equal variances assumed	4.615	.121	-3.517	3	.0390	-.2251	.0640	-.4288	-.0214
12	LnXYLENEMP	Equal variances assumed	.334	.594	3.033	4	.0387	.3805	.1254	.0322	.7287
13	LnXYLENEO	Equal variances assumed	.373	.575	3.823	4	.0187	.4360	.1140	.1194	.7527
14	LnHEXANEN	Equal variances assumed	.054	.827	-3.642	4	.0219	-.2541	.0698	-.4478	-.0604
15	LnTCDF2378	Equal variances assumed	.117	.755	6.399	3	.0077	1.3111	.2049	.6590	1.9633
16	LnKMTEQwho	Equal variances assumed	.000	.985	3.236	3	.0480	1.0957	.3386	.0180	2.1733

Group Statistics comparison of Baseline 2017 and Baseline 2019

		N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
		Sample		Sample		Sample		Sample		Sample	
		Base17	Base19	Base17	Base19	Base17	Base19	Base17	Base19	Base17	Base19
1	LnCO	3	3	5.3789	5.7167	.01329	.02945	.00767	.01700	216.8	303.9
2	LnNOx	3	3	6.8748	6.3900	.04600	.04831	.02656	.02789	967.5	595.9
3	LnNH4	3	3	2.2655	1.7618	.19070	.09296	.11010	.05367	9.64	5.82
4	LnAs	3	3	-.7233	.6044	.52985	.07704	.30591	.04448	0.49	1.83
5	LnCd	3	3	-1.6291	-.6999	.26298	.10476	.15183	.06048	0.20	0.50
6	LnCob	3	3	-1.5765	-.7871	.33408	.11024	.19288	.06365	0.21	0.46
7	LnFe	3	3	5.0095	5.9314	.04921	.09945	.02841	.05741	149.8	376.7
8	LnMo	3	3	1.2344	1.9622	.20475	.13978	.11821	.08070	3.44	7.11
9	LnSr	3	3	1.0724	2.1257	.40184	.23148	.23200	.13365	2.92	8.38
10	LnTi	3	3	2.1627	2.8948	.05813	.13649	.03356	.07880	8.69	18.08
11	LnBNZEPYRN	2	3	-.5762	-.3511	.10163	.04700	.07186	.02714	0.56	0.70
12	LnXYLENEMP	3	3	4.6994	4.3189	.17988	.12183	.10385	.07034	109.9	75.11
13	LnXYLENEO	3	3	3.9057	3.4697	.16193	.11313	.09349	.06532	49.68	32.13
14	LnHEXANEN	3	3	3.6846	3.9387	.08931	.08144	.05156	.04702	39.83	51.35
15	LnTCDF2378	2	3	3.2883	1.9771	.18409	.24215	.13017	.13980	26.80	7.22
16	LnKMTEQwho	2	3	3.9262	2.8305	.36643	.37318	.25910	.21546	50.71	16.95

Independent Samples Test comparing Baseline 2017 vs LCF 2019

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
										Lower	Upper
1	LnCO	0.552	0.499	-17.732	4.00	0.000	-0.162	0.009	-0.188	-0.137	
2	LnNOx	1.300	0.318	4.392	4.00	0.012	0.218	0.050	0.080	0.356	
3	LnSOx	1.414	0.300	5.007	4.00	0.007	0.520	0.104	0.232	0.809	
4	LnHg	.318	.612	-7.020	3	.006	-.48452	.06902	-.70418	-.26486	
5	LnMo	7.492	.072	-4.423	2.028	.046	-.52474	.11863	-1.02840	-.02107	
6	LnSr	4.695	.119	-5.971	3	.009	-1.79575	.30076	-2.75289	-.83860	
7	LnSn	2.962	.184	6.706	3	.007	1.40071	.20888	.73596	2.06545	
8	LnTi	3.364	.164	-21.117	3	.000	-1.48710	.07042	-1.71121	-1.26299	
9	LnETHBENZ	4.660	0.120	3.555	3.00	0.038	0.712	0.200	0.075	1.349	
10	LnXYLENEMP	1.300	0.318	5.655	4.00	0.005	0.637	0.113	0.324	0.950	
11	LnHEXANEN	0.058	0.825	-8.632	3.00	0.003	-0.695	0.081	-0.951	-0.439	
12	LnHEPTANE	1.672	0.287	5.115	3.00	0.014	0.176	0.034	0.066	0.285	
13	LnPROPENE	0.745	0.452	15.227	3.00	0.001	0.283	0.019	0.224	0.343	

Group Statistics comparison of Baseline 2017 and LCF 2019

	N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
	Sample		Sample		Sample		Sample		Sample	
	Base17	LCF19	Base17	LCF19	Base17	LCF19	Base17	LCF19	Base17	LCF19
1 LnCO	3	3	5.379	5.541	0.0133	0.0086	0.0077	0.0050	216.8	255.0
2 LnNOx	3	3	6.875	6.657	0.0460	0.0727	0.0266	0.0420	967.5	778.0
3 LnSOx	3	3	6.489	5.969	0.1558	0.0900	0.0900	0.0520	658.0	391.1
4 LnHg	3	2	1.3397	1.8242	.08460	.05325	.04884	.03766	3.818	6.198
5 LnMo	3	2	1.2344	1.7591	.20475	.01409	.11821	.00997	3.436	5.807
6 LnSr	3	2	1.0724	2.8681	.40184	.05178	.23200	.03662	2.922	17.604
7 LnSn	3	2	3.5657	2.1650	.16707	.31819	.09646	.22500	35.364	8.715
8 LnTi	3	2	2.1627	3.6498	.05813	.10533	.03356	.07448	8.695	38.468
9 LnETHBENZ	3	2	3.997	3.285	0.2659	0.0543	0.1535	0.0384	54.4	26.7
10 LnXYLENEMP	3	3	4.699	4.062	0.1799	0.0756	0.1039	0.0436	109.9	58.1
11 LnHEXANEN	3	2	3.685	4.380	0.0893	0.0859	0.0516	0.0607	39.8	79.8
12 LnHEPTANE	3	2	3.552	3.376	0.0421	0.0266	0.0243	0.0188	34.9	29.2
13 LnPROPENE	3	2	7.502	7.219	0.0224	0.0155	0.0129	0.0110	1812	1365

Independent Means Test Results comparison Baseline 2017 vs LCF 2020

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper	
1	LnPM10	Equal variances assumed	3.13	0.152	-3.55	4.00	0.024	-0.457	0.129	-0.814	-0.100
2	LnBa	Equal variances not assumed	4.69	0.096	5.90	2.06	0.026	0.567	0.096	0.165	0.968
3	LnFe	Equal variances not assumed	5.13	0.086	-4.77	2.08	0.038	-0.973	0.204	-1.819	-0.127
4	LnMo	Equal variances assumed	0.38	0.571	-4.65	4.00	0.010	-0.705	0.152	-1.126	-0.284
5	LnAg	Equal variances assumed	3.50	0.135	6.73	4.00	0.003	1.927	0.286	1.132	2.721
6	LnSr	Equal variances assumed	1.81	0.249	-4.82	4.00	0.009	-1.262	0.262	-1.989	-0.535
7	LnTi	Equal variances assumed	5.02	0.088	-3.91	4.00	0.017	-0.602	0.154	-1.030	-0.175
8	LnTRICBP	Equal variances not assumed	6.48	0.084	22.74	2.16	0.001	0.735	0.032	0.606	0.865
9	LnTCDF2378	Equal variances assumed	1.75	0.277	5.85	3.00	0.010	1.624	0.277	0.741	2.507
10	LnTCDF	Equal variances assumed	0.69	0.466	3.18	3.00	0.050	0.748	0.235	-0.001	1.498
11	LnPCDF	Equal variances assumed	1.46	0.314	4.02	3.00	0.028	1.887	0.470	0.393	3.381
12	LnKMTEQwho	Equal variances assumed	0.08	0.798	5.95	3.00	0.009	2.070	0.348	0.963	3.177

Group Statistics comparing Baseline 2017 vs LCF 2020

	N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
	Sample		Sample		Sample		Sample		Sample	
	Base17	LCF20	Base17	LCF20	Base17	LCF20	Base17	LCF20	Base17	LCF20
1 LnPM10	3.0	3.0	2.899	3.356	0.206	0.084	0.119	0.049	18.1	28.7
2 LnBa	3.0	3.0	3.081	2.514	0.020	0.165	0.012	0.095	21.8	12.4
3 LnFe	3.0	3.0	5.009	5.983	0.049	0.350	0.028	0.202	149.8	396.5
4 LnMo	3.0	3.0	1.234	1.939	0.205	0.165	0.118	0.095	3.4	7.0
5 LnAg	3.0	3.0	0.600	-1.327	0.134	0.477	0.077	0.276	1.8	0.3
6 LnSr	3.0	3.0	1.072	2.334	0.402	0.210	0.232	0.121	2.9	10.3
7 LnTi	3.0	3.0	2.163	2.765	0.058	0.260	0.034	0.150	8.7	15.9
8 LnTRICBP	2.0	3.0	1.670	0.934	0.009	0.055	0.006	0.032	5.3	2.5
9 LnTCDF2378	2.0	3.0	3.288	1.665	0.184	0.349	0.130	0.201	26.8	5.3
10 LnTCDF	2.0	3.0	7.222	6.474	0.133	0.302	0.094	0.174	1370	648
11 LnPCDF	2.0	3.0	5.430	3.543	0.652	0.429	0.461	0.248	228.2	34.6
12 LnKMTEQwho	2.0	3.0	3.926	1.856	0.366	0.388	0.259	0.224	50.7	6.4

Independent Samples Test comparison Baseline 2019 vs LCF 2019

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper	
1	LnCO	Equal variances assumed	2.182	0.214	9.916	4.0	0.0006	0.1757	0.0177	0.1265	0.2248
2	LnNOx	Equal variances assumed	1.055	0.362	-5.293	4.0	0.0061	-0.2667	0.0504	-0.4066	-0.1268
3	LnSOx	Equal variances assumed	2.250	0.208	4.002	4.0	0.0161	0.4547	0.1136	0.1392	0.7702
4	LnHg	Equal variances not assumed	48.90	0.01	-11.45	1.09	0.045	-0.44132	0.03853	-0.84131	-0.04132
5	LnAl	Equal variances assumed	1.40	0.32	-3.01	3.00	0.057	-0.57767	0.19185	-1.18822	0.03289
6	LnSb	Equal variances assumed	0.13	0.74	-12.61	3.00	0.001	-0.18871	0.01497	-0.23635	-0.14107
7	LnAs	Equal variances assumed	0.95	0.40	7.55	3.00	0.005	0.48231	0.06387	0.27903	0.68559
8	LnBe	Equal variances assumed	0.13	0.74	41.12	3.00	0.000	0.61552	0.01497	0.56788	0.66316
9	LnB	Equal variances assumed	2.23	0.23	6.18	3.00	0.009	0.64207	0.10397	0.31119	0.97295
10	LnCa	Equal variances assumed	1.75	0.28	-3.62	3.00	0.036	-0.75773	0.20907	-1.42308	-0.09239
11	LnCd	Equal variances assumed	3.95	0.14	9.00	3.00	0.003	0.72771	0.08089	0.47028	0.98513
12	LnCob	Equal variances assumed	1.85	0.27	4.40	3.00	0.022	0.39196	0.08911	0.10838	0.67554
13	LnP	Equal variances assumed	0.13	0.74	34.35	3.00	0.000	0.51418	0.01497	0.46654	0.56182
14	LnSe	Equal variances assumed	1.72	0.28	6.16	3.00	0.009	0.57670	0.09359	0.27886	0.87453
15	LnSr	Equal variances assumed	1.42	0.32	-4.25	3.00	0.024	-0.74241	0.17468	-1.29833	-0.18650
16	LnSn	Equal variances assumed	0.86	0.42	7.10	3.00	0.006	1.64282	0.23128	0.90678	2.37885
17	LnTi	Equal variances assumed	0.55	0.51	-6.52	3.00	0.007	-0.75507	0.11589	-1.12389	-0.38625
18	LnETHBENZ	Equal variances assumed	0.816	0.433	4.642	3.0	0.0188	0.3298	0.0711	0.1037	0.5559
19	LnXYLENEMP	Equal variances assumed	0.468	0.532	3.100	4.0	0.0362	0.2566	0.0828	0.0268	0.4864
20	LnHEXANEN	Equal variances assumed	0.000	0.993	-5.821	3.0	0.0101	-0.4408	0.0757	-0.6818	-0.1998

Group Statistics comparison Baseline 2019 vs LCF 2019

		N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
		Sample		Sample		Sample		Sample		Sample	
		Base19	LCF19	Base19	LCF19	Base19	LCF19	Base19	LCF19	Base19	LCF19
1	LnCO	3	3	5.717	5.541	0.0294	0.0086	0.0170	0.0050	303.9	255.0
2	LnNOx	3	3	6.390	6.657	0.0483	0.0727	0.0279	0.0420	595.9	778.0
3	LnSOx	3	3	6.424	5.969	0.1750	0.0900	0.1010	0.0520	616.3	391.1
4	LnHg	3	2	1.383	1.824	0.0141	0.0533	0.0082	0.0377	3.986	6.198
5	LnAl	3	2	6.073	6.651	0.2479	0.0980	0.1431	0.0693	433.9	773.2
6	LnSb	3	2	0.701	0.890	0.0152	0.0185	0.0088	0.0131	2.017	2.436
7	LnAs	3	2	0.604	0.122	0.0770	0.0531	0.0445	0.0375	1.830	1.130
8	LnBe	3	2	-1.058	-1.674	0.0152	0.0185	0.0088	0.0131	0.347	0.188
9	LnB	3	2	4.082	3.440	0.1389	0.0185	0.0802	0.0131	59.245	31.175
10	LnCa	3	2	8.583	9.341	0.2752	0.0768	0.1589	0.0543	5343	11398
11	LnCd	3	2	-0.700	-1.428	0.1048	0.0401	0.0605	0.0283	0.497	0.240
12	LnCob	3	2	-0.787	-1.179	0.1102	0.0654	0.0636	0.0463	0.455	0.308
13	LnP	3	2	5.042	4.528	0.0152	0.0185	0.0088	0.0131	154.8	92.6
14	LnSe	3	2	1.496	0.919	0.1245	0.0227	0.0719	0.0160	4.464	2.508
15	LnSr	3	2	2.126	2.868	0.2315	0.0518	0.1336	0.0366	8.379	17.604
16	LnSn	3	2	3.808	2.165	0.2137	0.3182	0.1234	0.2250	45.052	8.715
17	LnTi	3	2	2.895	3.650	0.1365	0.1053	0.0788	0.0745	18.079	38.468
18	LnETHBENZ	3	2	3.615	3.285	0.0873	0.0543	0.0504	0.0384	37.1	26.7
19	LnXYLENEMP	3	3	4.319	4.062	0.1218	0.0756	0.0703	0.0436	75.1	58.1
20	LnHEXANEN	3	2	3.939	4.380	0.0814	0.0859	0.0470	0.0607	51.4	79.8

Independent Samples Test comparing Baseline 2019 vs LCF 2020

		Levene's Test for		t-test for Equality of Means							
		Equality of Variances		t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
		F	Sig.						Lower	Upper	
1	LnHg	Equal variances not assumed	11.527	0.027	4.672	2.01	0.0425	0.80583	0.17248	0.06689	1.54478
2	LnSb	Equal variances not assumed	9.527	0.037	11.190	2.01	0.0078	2.43100	0.21724	1.49921	3.36279
3	LnAs	Equal variances assumed	2.225	0.210	7.180	4.00	0.0020	0.92049	0.12821	0.56453	1.27645
4	LnBa	Equal variances assumed	0.072	0.802	6.052	4.00	0.0038	0.76044	0.12565	0.41158	1.10930
5	LnBe	Equal variances not assumed	8.860	0.041	12.103	2.07	0.0060	0.83699	0.06915	0.54832	1.12566
6	LnB	Equal variances assumed	0.101	0.767	-5.733	4.00	0.0046	-0.73925	0.12896	-1.09729	-0.38121
7	LnBl	Equal variances not assumed	8.860	0.041	16.457	2.07	0.0032	1.13809	0.06915	0.84943	1.42676
8	LnCd	Equal variances assumed	2.347	0.200	3.118	4.00	0.0356	0.83100	0.26649	0.09109	1.57090
9	LnMg	Equal variances assumed	0.126	0.741	-3.811	4.00	0.0189	-0.64162	0.16836	-1.10906	-0.17418
10	LnP	Equal variances not assumed	8.860	0.041	11.972	2.07	0.0061	0.82794	0.06915	0.53927	1.11661
11	LnSe	Equal variances assumed	1.653	0.268	12.433	4.00	0.0002	0.94155	0.07573	0.73129	1.15180
12	LnAg	Equal variances assumed	0.284	0.622	3.713	4.00	0.0206	1.66727	0.44905	0.42052	2.91402
13	LnNa	Equal variances assumed	2.859	0.166	-12.088	4.00	0.0003	-1.58052	0.13075	-1.94353	-1.21751
14	LnTe	Equal variances not assumed	8.860	0.041	-4.587	2.07	0.0418	-0.31719	0.06915	-0.60586	-0.02853
15	LnSn	Equal variances assumed	0.008	0.934	2.998	4.00	0.0400	0.51111	0.17051	0.03771	0.98451
16	LnZn	Equal variances assumed	0.206	0.673	3.221	4.00	0.0323	1.12587	0.34957	0.15529	2.09644
17	LnHXCBP	Equal variances assumed	2.890	0.164	3.083	4.00	0.0368	1.03344	0.33519	0.10281	1.96408
18	LnNONACBP	Equal variances assumed	0.195	0.689	-6.361	3.00	0.0079	-1.54081	0.24223	-2.31170	-0.76993
19	LnDECBP	Equal variances not assumed	7.163	0.075	-41.135	2.03	0.0005	-2.38855	0.05807	-2.63448	-2.14261
20	LnNAPHLENE	Equal variances assumed	0.100	0.768	-15.232	4.00	0.0001	-1.10803	0.07274	-1.30999	-0.90606
21	LnACENPHLN	Equal variances assumed	3.411	0.138	-4.290	4.00	0.0127	-0.50391	0.11745	-0.83002	-0.17781
22	LnACENATHN	Equal variances not assumed	5.154	0.086	3.654	2.59	0.0451	0.59597	0.16309	0.02696	1.16498
23	LnPHENATHN	Equal variances assumed	0.440	0.543	3.852	4.00	0.0183	0.25651	0.06659	0.07162	0.44140
24	LnBENZANTH	Equal variances assumed	0.303	0.611	-9.570	4.00	0.0007	-0.45462	0.04750	-0.58651	-0.32272
25	LnBNZAPYRN	Equal variances assumed	0.024	0.885	4.725	4.00	0.0091	0.96694	0.20466	0.39872	1.53517
26	LnINDEPYRN	Equal variances not assumed	8.349	0.045	25.505	2.15	0.0010	0.69282	0.02716	0.58338	0.80226
27	LnMTLNAPH1	Equal variances assumed	0.001	0.981	-8.051	4.00	0.0013	-0.53864	0.06691	-0.72440	-0.35287
28	LnPCDF	Equal variances assumed	0.007	0.938	3.361	4.00	0.0283	1.17963	0.35094	0.20526	2.15399
29	LnKMTEQwho	Equal variances assumed	0.042	0.847	3.133	4.00	0.0351	0.97404	0.31090	0.11084	1.83724

Group Statistics comparison Baseline 2019 vs LCF 2020

		N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
		Sample		Sample		Sample		Sample		Sample	
		Base19	LCF20	Base19	LCF20	Base19	LCF20	Base19	LCF20	Base19	LCF20
1	LnHg	3	3	1.3829	.5770	.01412	.29840	.00815	.17228	4.0	1.8
2	LnSb	3	3	.7015	-1.7295	.01523	.37597	.00879	.21706	2.0	0.2
3	LnAs	3	3	.6044	-.3161	.07704	.20827	.04448	.12025	1.8	0.7
4	LnBa	3	3	3.2747	2.5143	.14188	.16502	.08191	.09528	26.4	12.4
5	LnBe	3	3	-1.0583	-1.8953	.01523	.11881	.00879	.06859	0.35	0.15
6	LnB	3	3	4.0817	4.8209	.13888	.17494	.08018	.10100	59.2	124.1
7	LnBl	3	3	.0313	-1.1068	.01523	.11881	.00879	.06859	1.0	0.3
8	LnCd	3	3	-.6999	-1.5309	.10476	.44954	.06048	.25954	0.5	0.2
9	LnMg	3	3	5.0878	5.7294	.23306	.17526	.13456	.10119	162	308
10	LnP	3	3	5.0419	4.2140	.01523	.11881	.00879	.06859	154.8	67.6
11	LnSe	3	3	1.4960	.5545	.12453	.04118	.07190	.02378	4.5	1.7
12	LnAg	3	3	.3407	-1.3266	.61405	.47736	.35452	.27560	1.41	0.27
13	LnNa	3	3	5.7614	7.3419	.04856	.22119	.02803	.12771	317.8	1543.7
14	LnTe	3	3	-.1975	.1197	.01523	.11881	.00879	.06859	0.8	1.1
15	LnSn	3	3	3.8078	3.2967	.21368	.20385	.12337	.11769	45.1	27.0
16	LnZn	3	3	3.6867	2.5609	.48109	.36764	.27776	.21226	39.9	12.9
17	LnHXCBP	3	3	-.4964	-1.5298	.57252	.09629	.33055	.05559	0.6	0.2
18	LnNONACBP	2	3	-5.7234	-4.1826	.30368	.24394	.21473	.14084	0.003	0.015
19	LnDECBP	2	3	-5.1751	-2.7866	.00750	.10015	.00531	.05782	0.006	0.062
20	LnNAPHELENE	3	3	4.0212	5.1292	.08066	.09679	.04657	.05588	55.8	168.9
21	LnACENPHLN	3	3	.6971	1.2010	.19785	.04735	.11423	.02734	2.0	3.3
22	LnACENATHN	3	3	-1.3018	-1.8978	.10213	.26337	.05896	.15205	0.27	0.15
23	LnPHENATHN	3	3	2.3867	2.1302	.09164	.07005	.05291	.04044	10.9	8.4
24	LnBENZANTH	3	3	-2.0398	-1.5852	.06905	.04475	.03987	.02584	0.130	0.205
25	LnBNZAPYRN	3	3	-2.4708	-3.4377	.27057	.22902	.15621	.13223	0.085	0.032
26	LnINDEPYRN	3	3	-3.4610	-4.1539	.00893	.04620	.00515	.02667	0.031	0.016
27	LnMTLNAPH1	3	3	2.1585	2.6971	.08088	.08299	.04670	.04792	8.7	14.8
28	LnPCDF	3	3	4.7229	3.5432	.43046	.42916	.24853	.24777	112.5	34.6
29	LnKMTEQwho	3	3	2.8305	1.8565	.37318	.38822	.21546	.22414	17.0	6.4

Independent Samples Test comparison of LCFs 2019 vs 2020

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper	
1	LnHg	Equal variances assumed	5.309	0.105	5.563	3	0.011	1.24715	0.22418	0.53371	1.96060
2	LnSb	Equal variances not assumed	5.664	0.098	12.047	2	0.007	2.61971	0.21746	1.69050	3.54892
3	LnBa	Equal variances assumed	1.459	0.314	4.900	3	0.016	0.62303	0.12715	0.21839	1.02768
4	LnB	Equal variances assumed	2.081	0.245	-10.564	3	0.002	-1.38132	0.13075	-1.79744	-0.96520
5	LnBl	Equal variances assumed	5.195	0.107	7.077	3	0.006	0.63047	0.08909	0.34694	0.91400
6	LnP	Equal variances assumed	5.195	0.107	3.522	3	0.039	0.31376	0.08909	0.03023	0.59728
7	LnSe	Equal variances assumed	1.847	0.267	11.076	3	0.002	0.36485	0.03294	0.26002	0.46968
8	LnNa	Equal variances assumed	.120	0.752	-9.592	3	0.002	-1.80843	0.18853	-2.40842	-1.20845
9	LnSr	Equal variances assumed	5.129	0.108	3.359	3	0.044	0.53419	0.15905	0.02802	1.04036
10	LnSn	Equal variances assumed	1.120	0.368	-5.001	3	0.015	-1.13170	0.22630	-1.85188	-0.41152
11	LnTi	Equal variances assumed	1.969	0.255	4.383	3	0.022	0.88462	0.20183	0.24231	1.52693

Group Statistics comparison of LCFs 2019 vs 2020

	N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
	Sample		Sample		Sample		Sample		Sample	
	LCF19	LCF20	LCF19	LCF20	LCF19	LCF20	LCF19	LCF20	LCF19	LCF20
1 LnHg	2	3	1.8242	0.5770	0.0533	0.2984	0.0377	0.1723	6.20	1.78
2 LnSb	2	3	0.8902	-1.7295	0.0185	0.3760	0.0131	0.2171	2.44	0.18
3 LnBa	2	3	3.1373	2.5143	0.0611	0.1650	0.0432	0.0953	23.04	12.36
4 LnB	2	3	3.4396	4.8209	0.0185	0.1749	0.0131	0.1010	31.17	124.08
5 LnBI	2	3	-0.4763	-1.1068	0.0185	0.1188	0.0131	0.0686	0.62	0.33
6 LnP	2	3	4.5278	4.2140	0.0185	0.1188	0.0131	0.0686	92.55	67.63
7 LnSe	2	3	0.9193	0.5545	0.0227	0.0412	0.0160	0.0238	2.51	1.74
8 LnNa	2	3	5.5335	7.3419	0.1735	0.2212	0.1227	0.1277	253.03	1543.71
9 LnSr	2	3	2.8681	2.3339	0.0518	0.2102	0.0366	0.1214	17.60	10.32
10 LnSn	2	3	2.1650	3.2967	0.3182	0.2039	0.2250	0.1177	8.71	27.02
11 LnTi	2	3	3.6498	2.7652	0.1053	0.2603	0.0745	0.1503	38.47	15.88

Independent Samples Test comparing LCF 2019 with 2017 and 2019 Baseline

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper	
1	LnTSP	Equal variances assumed	.899	.380	-2.525	6	.04496	-.64654	.25601	-1.27298	-.02010
2	LnSOx	Equal variances assumed	1.804	.221	5.011	7	.00155	.48749	.09728	.25746	.71752
3	LnTHC	Equal variances not assumed	14.715	.006	2.771	5.165	.03798	.40762	.14712	.03304	.78220
4	LnHg	Equal variances assumed	.025	.879	-9.736	6	.00007	-.46292	.04755	-.57927	-.34657
5	LnSb	Equal variances assumed	.133	.740	-12.606	3	.00108	-.18871	.01497	-.23635	-.14107
6	LnBe	Equal variances assumed	.133	.740	41.117	3	.00003	.61552	.01497	.56788	.66316
7	LnCa	Equal variances assumed	1.746	.278	-3.624	3	.03614	-.75773	.20907	-1.42308	-.09239
8	LnMn	Equal variances not assumed	4.181	.087	-4.389	5.002	.00709	-.44086	.10045	-.69906	-.18266
9	LnP	Equal variances assumed	.133	.740	34.347	3	.00005	.51418	.01497	.46654	.56182
10	LnAg	Equal variances assumed	.142	.720	4.216	6	.00559	1.41156	.33484	.59223	2.23089
11	LnSr	Equal variances not assumed	5.025	.066	-4.758	5.184	.00461	-1.26908	.26675	-1.94751	-.59065
12	LnSn	Equal variances assumed	.446	.529	7.872	6	.00022	1.52176	.19331	1.04875	1.99477
13	LnTi	Equal variances not assumed	17.379	.006	-6.097	6.000	.00089	-1.12108	.18387	-1.57100	-.67117
14	LnVCMONMR	Equal variances assumed	.	.	3.267	5	.02226	.52615	.16103	.11220	.94009
15	LnETHCL	Equal variances assumed	.	.	76.514	1	.00832	.72198	.00944	.60209	.84188
16	LnCB	Equal variances assumed	.	.	4.464	3	.02094	.36010	.08067	.10337	.61684
17	LnETHBENZ	Equal variances assumed	1.483	.269	2.540	6	.04411	.52085	.20510	.01900	1.02271
18	LnXYLENEMP	Equal variances assumed	2.630	.149	2.942	7	.02165	.44683	.15188	.08768	.80598
19	LnHEXANEN	Equal variances assumed	1.355	.289	-4.663	6	.00346	-.56786	.12177	-.86582	-.26990
20	LnPROPENE	Equal variances not assumed	4.749	.072	2.706	5.314	.03992	.16434	.06074	.01094	.31775

Group Statistics comparison Combined Baseline 2017 and 2019 with LCF 2019

		N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
		Sample		Sample		Sample		Sample		Sample	
		Baseline	LCF2019	Baseline	LCF2019	Baseline	LCF2019	Baseline	LCF2019	Baseline	LCF2019
1	LnTSP	6	2	3.5775	4.2240	.27897	.44806	.11389	.31682	35.784	68.308
2	LnSOx	6	3	6.4565	5.9690	.15249	.09004	.06225	.05199	636.8	391.1
3	LnTHC	6	3	2.2969	1.8892	.35740	.03269	.14591	.01888	9.9	6.6
4	LnHg	6	2	1.3613	1.8242	.05918	.05325	.02416	.03766	3.9	6.2
5	LnSb	3	2	.7015	.8902	.01523	.01852	.00879	.01310	2.0	2.4
6	LnBe	3	2	-1.0583	-1.6738	.01523	.01852	.00879	.01310	0.3	0.2
7	LnCa	3	2	8.5835	9.3412	.27519	.07678	.15888	.05429	5342.7	11398.3
8	LnMn	6	2	2.5217	2.9626	.24604	.00195	.10044	.00138	12.5	19.3
9	LnP	3	2	5.0419	4.5278	.01523	.01852	.00879	.01310	154.8	92.6
10	LnAg	6	2	.4705	-.9411	.42211	.34382	.17232	.24312	1.6	0.4
11	LnSr	6	2	1.5991	2.8681	.64721	.05178	.26422	.03662	4.9	17.6
12	LnSn	6	2	3.6868	2.1650	.21683	.31819	.08852	.22500	39.9	8.7
13	LnTi	6	2	2.5287	3.6498	.41178	.10533	.16811	.07448	12.5	38.5
14	LnVCMONMR	6	1	3.6789	3.1527	.14909	.	.06086	.	39.6	23.4
15	LnETHCL	2	1	1.8038	1.0818	.00770	.	.00545	.	6.1	3.0
16	LnCB	4	1	2.8778	2.5177	.07215	.	.03608	.	17.8	12.4
17	LnETHBENZ	6	2	3.8057	3.2849	.27409	.05430	.11190	.03839	45.0	26.7
18	LnXYLENEMP	6	3	4.5091	4.0623	.24961	.07558	.10190	.04364	90.8	58.1
19	LnHEXANEN	6	2	3.8117	4.3796	.15879	.08590	.06483	.06074	45.2	79.8
20	LnPROPENE	6	2	7.3832	7.2188	.14633	.01554	.05974	.01099	1608.7	1364.9

Independent Samples Test comparing LCF 2020 with 2017 and 2019 Baseline

		Levene's Test for Equality of Variances		t-test for Equality of Means							
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference		
									Lower	Upper	
1	LnHg	Equal variances not assumed	15.325	.006	4.508	2.079	.043	.78423	.17397	.06235	1.50612
2	LnSb	Equal variances not assumed	9.527	.037	11.190	2.007	.008	2.43100	.21724	1.49921	3.36279
3	LnBa	Equal variances assumed	.002	.964	6.369	7	.000	.66349	.10418	.41715	.90982
4	LnBe	Equal variances not assumed	8.860	.041	12.103	2.066	.006	.83699	.06915	.54832	1.12566
5	LnB	Equal variances assumed	1.289	.294	-2.630	7	.034	-.67266	.25580	-1.27753	-.06779
6	LnMg	Equal variances assumed	.126	.741	-3.811	4	.019	-.64162	.16836	-1.10906	-.17418
7	LnP	Equal variances assumed	8.860	.041	11.972	4	.000	.82794	.06915	.63594	1.01994
8	LnSe	Equal variances assumed	2.919	.138	2.756	6	.033	.75458	.27384	.08452	1.42463
9	LnAg	Equal variances assumed	.037	.853	5.794	7	.001	1.79704	.31014	1.06368	2.53040
10	LnNa	Equal variances assumed	2.859	.166	-12.088	4	.000	-1.58052	.13075	-1.94353	-1.21751
11	LnSr	Equal variances not assumed	4.250	.078	-2.527	6.598	.041	-.73489	.29077	-1.43102	-.03876
12	LnTe	Equal variances not assumed	8.860	.041	-4.587	2.066	.042	-.31719	.06915	-.60586	-.02853
13	LnZn	Equal variances assumed	.125	.738	3.190	5	.024	1.01794	.31914	.19758	1.83831
14	LnPECBP	Equal variances not assumed	14.278	.009	4.542	4.254	.009	1.28801	.28358	.51886	2.05716
15	LnHXCBP	Equal variances assumed	3.728	.102	3.658	6	.011	1.23490	.33755	.40894	2.06085
16	LnNONACBP	Equal variances assumed	.195	.689	-6.361	3	.008	-1.54081	.24223	-2.31170	-.76993
17	LnDECBP	Equal variances not assumed	7.163	.075	-41.135	2.034	.001	-2.38855	.05807	-2.63448	-2.14261
18	LnNAPHELENE	Equal variances assumed	1.496	.267	-5.520	6	.001	-.99236	.17978	-1.43227	-.55246
19	LnBNZAPYRN	Equal variances assumed	.024	.885	4.725	4	.009	.96694	.20466	.39872	1.53517
20	LnINDEPYRN	Equal variances not assumed	8.349	.045	25.505	2.149	.001	.69282	.02716	.58338	.80226
21	LnMTLNAPH1	Equal variances assumed	.001	.981	-8.051	4	.001	-.53864	.06691	-.72440	-.35287
22	LnPCDF1	Equal variances assumed	2.117	.205	2.971	5	.031	1.04845	.35288	.14133	1.95556
23	LnTCDF	Equal variances assumed	.119	.742	2.500	6	.047	.53449	.21378	.01138	1.05760
24	LnPCDF	Equal variances assumed	.234	.646	3.693	6	.010	1.46258	.39606	.49346	2.43170
25	LnTCDD	Equal variances not assumed	4.268	.084	4.244	4.168	.012	1.65363	.38965	.58877	2.71849
26	LnKMQTEQwho	Equal variances assumed	1.199	.316	3.227	6	.018	1.41231	.43765	.34141	2.48320

Group Statistics comparison Combined Baseline 2017 and 2019 with LCF 2020

		N		Mean		Std. Deviation		Std. Error Mean		Geometric Mean	
		Sample		Sample		Sample		Sample		Sample	
		Baseline	LCF2020	Baseline	LCF2020	Baseline	LCF2020	Baseline	LCF2020	Baseline	LCF2020
1	LnHg	6	3	1.3613	.5770	.05918	.29840	.02416	.17228	3.901	1.781
2	LnSb	3	3	.7015	-1.7295	.01523	.37597	.00879	.21706	2.0	0.2
3	LnBa	6	3	3.1778	2.5143	.13962	.16502	.05700	.09528	24.0	12.4
4	LnBe	3	3	-1.0583	-1.8953	.01523	.11881	.00879	.06859	0.3	0.2
5	LnB	6	3	4.1483	4.8209	.41349	.17494	.16881	.10100	63.3	124.1
6	LnMg	3	3	5.0878	5.7294	.23306	.17526	.13456	.10119	162.0	307.8
7	LnP	3	3	5.0419	4.2140	.01523	.11881	.00879	.06859	154.8	67.6
8	LnSe	5	3	1.3090	.5545	.45831	.04118	.20496	.02378	3.7	1.7
9	LnAg	6	3	.4705	-1.3266	.42211	.47736	.17232	.27560	1.6	0.3
10	LnNa	3	3	5.7614	7.3419	.04856	.22119	.02803	.12771	317.8	1543.7
11	LnSr	6	3	1.5991	2.3339	.64721	.21023	.26422	.12137	4.9	10.3
12	LnTe	3	3	-.1975	.1197	.01523	.11881	.00879	.06859	0.8	1.1
13	LnZn	4	3	3.5788	2.5609	.44820	.36764	.22410	.21226	35.8	12.9
14	LnPECBP	5	3	.7131	-.5749	.62409	.08691	.27910	.05018	2.0	0.6
15	LnHXCBP	5	3	-.2949	-1.5298	.56198	.09629	.25132	.05559	0.7	0.2
16	LnNONACBP	2	3	-5.7234	-4.1826	.30368	.24394	.21473	.14084	0.00	0.02
17	LnDECBP	2	3	-5.1751	-2.7866	.00750	.10015	.00531	.05782	0.01	0.06
18	LnNAPHELENE	5	3	4.1368	5.1292	.29363	.09679	.13131	.05588	62.6	168.9
19	LnBNZAPYRN	3	3	-2.4708	-3.4377	.27057	.22902	.15621	.13223	0.08	0.03
20	LnINDEPYRN	3	3	-3.4610	-4.1539	.00893	.04620	.00515	.02667	0.03	0.02
21	LnMTLNAPH1	3	3	2.1585	2.6971	.08088	.08299	.04670	.04792	8.7	14.8
22	LnPCDF1	5	2	-.5885	-1.6369	.46640	.13909	.20858	.09835	0.6	0.2
23	LnTCDF	5	3	7.0084	6.4739	.28820	.30160	.12889	.17413	1105.8	648.0
24	LnPCDF	5	3	5.0058	3.5432	.59084	.42916	.26423	.24777	149.3	34.6
25	LnTCDD	5	3	4.4389	2.7852	.86217	.09731	.38558	.05618	84.7	16.2
26	LnKMTEQwho	5	3	3.2688	1.8565	.68070	.38822	.30442	.22414	26.3	6.4

APPENDIX A

DATA REVIEW ISSUES

There are many steps between the extraction of samples from the stack and the publication of the test report. While every step of the process can be reviewed, it should be remembered that the test protocol was approved by NS Environment and it can be assumed that field procedures were satisfactory, with the exceptions noted in the previous section. Quality Assurance/Quality Control procedures were incorporated into the test program both for the field work and the analytical laboratory procedures. While the laboratory reports highlight limitations to their analytical results all procedures were assumed to be satisfactory and thus the anomalies identified in the laboratory need to be incorporated into any consideration of the data.

In the author's experience a quality assurance check of stack sampling report data is prudent. There is a large amount of data involved with any test. Sampling train operational data and process data are integrated with analytical results from the laboratory. This provides numerous opportunities for simple transcription mistakes. Having reviewed many stack sampling reports the author has identified that the procedures used to convert the mass of material identified in the samples to an emission concentration or emission rate from the process is the most likely to create problems. As such, this data reduction process is confirmed by re-calculating the emission concentration results based upon the mass of material the laboratory reports and the sample volumes reported by the stack testing firm. In addition, random checks of the various steps in the calculation of the test results are used to ensure that the sample volumes reported, and the stack flow data are correct. To support the re-calculation, all the laboratory data for each test run is entered into a standard data reduction spreadsheet, along with the cross-checked sample volumes and stack flows. Some of the facility operating data that allows one to distinguish between different operating conditions is entered into the spreadsheet along with reported moisture, oxygen, and stack temperature. The laboratory reported mass is then converted to concentration at a reference condition expressed as the stack gas dry volume in m³ at 25°C, 101.3 kPa, and 11% oxygen. The data is then ready for a comparison of the emission concentrations from different operating conditions to see if there are any differences.

The process of re-entering all the laboratory data into a standard form affords an opportunity to review every result and identify limitations in the results that could influence statistical comparisons between data sets. There are several situations that can influence statistical analyses of data sets and these are addressed in the following paragraphs.

Dealing with Low Concentrations in Samples

Sampling procedures are designed to collect sufficient material that the laboratory can determine the amount of a particular species in the sample. One way to ensure that there is enough material is to collect larger sample volumes than is called for by the methods. However, this might not always work and the laboratory will not be able to quantify the amount of the species in a sample. The laboratory then reports the results for that species as being something less than the laboratory detection limit. This number is derived using several criteria, and is included in the report flagged as an inconclusive result.

If the result cannot be quantified there are several ways to interpret the data. From a regulatory perspective, ie. a comparison of emissions to standards for enforcement purposes, the preferred approach would be to assume that the emissions are at the detection limit. This is a conservative approach because the emissions would be reported as being higher than measured. If, the calculation using the substitution indicates a potential issue with emissions the testing would be repeated, usually with a larger volume of gas being sampled. Another alternative that is used is to substitute zero for missing data, resulting in lower emission values. This is not conservative because there could still be contaminants released at concentrations between zero and the detection limit.

Unfortunately, missing data, or detection limit substitutions, introduce a lower bound to the data that has no statistical basis. Indeed, if one compares data from the same facility over a period of years, it is not unusual to see the detection limit decrease in later testing, and statistical analysis of those results can produce erroneous conclusions induced by laboratory performance, not the performance of the source.

The presence of below detection limit values is exacerbated when the laboratory must analyse several different samples from the same test to quantify the total released. Metals analyses require 3 samples to be analysed for each test for the bulk of the metals, and 5 samples must be analysed for mercury. Adding to the complexity are the results for “field blanks” which are used to correct metals results for the presence of contaminants in reagents or the filter. How should BDL values be incorporated into the results. Again we have options, ignore them, or include the values by substituting the DL for the BDL value.

In 2015 the US EPA OAQPS addressed the issue of dealing with BDL values²⁰ during the blank correction process for metals data, particularly for mercury data. The EPA’s recommendation was that if there were BDL values those values and detected quantities should be summed without regard for the sign. A similar procedure should thus be applied for front and back half analyses of metals data since Method 29 calls for the blank correction of the two halves to be done separately using the Field Reagent Blank data, before they are summed. A review of earlier results from the facility show that the blank correction procedure did not follow the US EPA Method 29 procedures.

For the purposes of this report, all 2019 and 2020 laboratory metal sampling results were recalculated without regard for the sign of the values, that is any values reported as BDL were included at that level. This results in higher emissions being used for the statistical tests than are reported in the stack test report. In the absence of detailed laboratory data for the 2017 test series, the BDL for the metal data were retained with negative signs to distinguish them.

Recognizing Matrix Interferences

laboratory analytical methods may need to be adjusted to address matrix interferences in the samples being analysed. These limitations frequently result in elevated estimated detection levels, which like low levels, limit the effectiveness of statistical analysis procedures since they introduce biases. If there are significant differences between results and some of the samples were subject to interferences this effect could explain the statistical results.

²⁰ [moreado.pdf \(epa.gov\)](#)

Blank Correction Procedures

It is common for test reports to present particulate data that has been corrected for the levels of solids found in the blank sampling system. The use of this “blank train” is a QA/QC adjunct that compensates for contaminants that may enter the sampling system during assembly, transport and use in the field, or contaminants present in the filter or liquids used in collecting the samples.

For US EPA Method 29 sampling, contamination in the train introduced by reagents etc. is supposed to be accounted for by measuring the species in both the reagents used and the filter (the method classifies these as field reagent blanks) and adjusting the sample masses by the quantities in the field reagent blank. If the field reagent blanks are not analysed there can be no correction.

During Brookfield testing, the Blank Trains were analysed to provide an indication of level of contaminants found in the sampling trains. As a QA/QC measure, if the Blank and Field samples are the same order of magnitude one might question the significance of the reported sample catch. Is it important, or does it just reflect the variability at the low end of the mass captured?

Organic compound measurements are not blank corrected according to conventions adopted in 1985 by Environment Canada. Organic results are frequently reported with BDL values which reduces the ability to statistically analyse the differences induced by low carbon fuel. Unlike the metals data, no substitution was used when dealing with the organic data; the results are presented as reported, and the BDL values limited the number of comparisons that can be completed. For VOCs and PAHs the quantity of the compounds emitted is low with test results being similar to the blank train results. For PCDD/F separate procedures were used to provide comparisons between the results and to the emission standard expressed as mass TEQ/Rm³. These procedures are discussed in the next section of this appendix.

Addressing PCDD/F Laboratory Results with No Detectable Quantities

Before discussing emissions data from the facility, it is appropriate to develop a method to express the emissions of PCDD/F. PCDD/F are comprised of many different individual congeners of chlorinated organics. Laboratories determine the mass of 17 specific congeners in samples, but rather than setting criteria for emissions of each congener, scientists have determined that a single value, the Toxic Equivalence [TEQ] is an appropriate measure. The TEQ is calculated by multiplying the mass of each of the 17 congeners by a specific factor that represents the toxicity of that congener compared to the toxicity of 2,3,7,8 tetrachlorinated dibenzo-*p*-dioxin. The resulting values is then summed for all the congeners to determine the TEQ. When analytical data for the dioxin like PCBs is available, the TEQ calculation is applied to those species as well and those results are summed with the PCDD/F results. The latter is the approach developed by the WHO in 2005 and TEQ values calculated in this manner are labelled TEQ_{WHO2005}. These are the TEQ values used in this report. Unfortunately, there is a minor stumbling block to the universal application of this approach.

Environmental data frequently contain values that are below the detection limits according to the authors of a 1994 paper²¹. It would not be unusual to see such values in water data or even in soil data particularly if large numbers of samples are collected from a site. The authors suggest that summary statistics of such large

²¹ Non-detect data in environmental investigations. <https://www.osti.gov/servlets/purl/10156972/>

studies must account for both detect and non-detect values. However, they also note that achieving satisfactory statistics is a function of how the data will be used. For instance, if the results are used to screen a site for remedial action, a detection limit well below the Screening Action Level, [SAL], will have little impact on decisions; however, if the detection level approaches the SAL further steps are required. Moreover, the problems posed by non-detects are more critical if one is trying to compare different populations, say samples from different sources, or even different portions of a process contributing to emissions.

In the late 1990s, during the development of the CCME Guidelines for PCDD/F²², laboratories seldom had to report limitations in quantifying PCDD/F. Improvements in combustion control and the addition of air pollution emission control systems have lowered PCDD/F emissions to the point where non-detectable levels of congeners are now present in many laboratory results. These are reported as non-detectable (ND) with the Estimated Detection Level (EDL) and Reportable Detection Level (RDL) being listed for each congener. The US EPA²³ stated that the sample specific EDL is a laboratory estimate of the concentration of a given analyte that would produce a signal with a peak height of at least 2.5 times (2.5x) the background noise signal level. This estimate is specific to a particular analysis of the sample and is affected by sample size, dilution, etc. The RDL is typically 10x the EDL.

If ND levels are reported, the historical approach has been to calculate the toxic equivalence of the sample, either considering the congener to be not present, or substituting the EDL for that congener in the calculation. Such substitution is required in Ontario as explained in the Ministry of Environment (MoE) Guideline A-8²⁴ and data is reported in that manner to the Province. However, the values reported by the laboratory are not always the EDL as defined above, occasionally the laboratory report values as the EMPC.

ALS reports define the EDL as the "*Estimated Detection Limit based on the measured background noise for this target in the sample*" and the EMPC as the "*Estimated Maximum Possible Concentration – elevated detection limit due to interference or positive id criterion failure*". EMPC is used for a result where a peak is detected that does not meet all the criteria for qualitative determination of the congener (most commonly the ion abundance ratio outside the allowed theoretical range of $\pm 15\%$)²⁵. It can be postulated that there were substances in the sample that interfered with obtaining a quantifiable result. The reported EMPC concentration represents an upper bound on the congener concentration.

The EMPC values can be substituted for the congener values in the test results, however this is not readily identifiable from the summary values issued by the laboratory. The summary results show the BDL values with the < sign, but one needs to go back into the laboratory detail report for each sample to determine if there were interferences that artificially elevated the reported BDL value. Typically large differences between identified BDL values might indicate the presence of interfering substances.

²² http://www.ccme.ca/files/Resources/air/dioxins_furans/waste_incinerators_coastal_pulp/d_and_f_standard_e.pdf

²³ US Environmental Protection Agency. n.d. "Clean Air Act National Stack Testing Guidance." Accessed 12 3, 2013. <http://www.epa.gov/compliance/resources/policies/monitoring/caa/stacktesting.pdf>.

²⁴ [Guideline A-8: Guideline for the Implementation of Canada-wide Standards for Emissions of Mercury | Ontario.ca](#)

²⁵ Laroo, C., Schenk, C., Sanchez, J., McDonald, J. et al., "Emissions of PCDD/Fs, PCBs, and PAHs from a Modern Diesel Engine Equipped with Selective Catalytic Reduction Filters," SAE Int. J. Engines 6(2):2013, doi: 10.4271/2013-01-1778.

With a high proportion of ND values in the data from the facility, concerns exist about the potential influence that various substitution procedures might have on the data variability. Helsel²⁶ suggests that the substitution approach creates a situation where the less precise data can have a large effect on the result particularly if the EDL is high. This is particularly a concern when calculating the $TEQ_{WHO2005}$ for emission data. If different samples show different congeners as being below the detection limit, substitution before calculating the TEQ is subject to more uncertainty, and comparisons between samples or sources will be meaningless. Helsel cites the work of several authors showing the inadequacy of the substitution process and recommends the use of the Kaplan-Meier (KM) procedure that is frequently used in survival analysis for computing the mean of right-hand censored data. Essentially the procedure generates the mean of the congener values times their respective TEF. The calculated mean can be multiplied by 17, the number of congeners considered in the TEQ calculation, provides a reliable prediction of the mean TEQ value for the test. The resulting mean is based upon parametric procedures that do not require transformations or assumptions about the specific distributional shape of the data. Further statistics such as the upper confidence limit of the mean can also be provided. Helsel provides a spreadsheet²⁷ that was used for this study.

Data reduction procedure for these test results was as follows:

1. The laboratory results, the mass for each congener [pg], were transcribed as presented complete with the designation of values below the detection limit. The ND identifier, a < symbol was replaced with a -ve sign to allow mathematical manipulation in the spreadsheet.
2. The [pg] mass was divided by the volume of gas sampled as determined from the standard meter volume, dry standard cubic meters [dscm]. The results being [pg/dscm].
3. The WHO₂₀₀₅ toxicity equivalence factor for each congener was then used to multiply the [pg/dscm] concentration. This approach retains both the identification of the congeners that were BDL - -ve sign - and the value of the detection limit.
4. These congener TEQ values were read into the Helsel spreadsheet. The non-detects were identified and assigned a flag, and the -ve sign was dropped from the values so they could be rank ordered for the statistical procedure. The spreadsheet then determines the statistics for the mean TEQ for the congeners in [pg $TEQ_{WHO2005}$ /dscm].

The one issue that cannot be addressed by the Helsel approach is laboratory results where none of the congeners are greater than the EDL or EMPC. This was not observed for this study. Helsel²⁸ suggests that point estimates in this case are inappropriate for parameters measured as single values. Determining the TEQ of such samples is more difficult and the author suggests that the only option is to substitute the reporting limit to provide a worst-case value of the total TEQ. It must be recognized that the true TEQ may be far lower than this value.

²⁶ Helsel, Dennis R. 2010. "Summing Nondetects: Incorporating Low-Level Contaminants in Risk Assessment." *Integrated Environmental Assessment and Management* (6): 361-366.

²⁷ Helsel, Dennis R. n.d. Accessed March 3, 2014. http://www.practicalstats.com/nada/downloads_files/KMStats15.xls.

²⁸ Helsel, Dennis R., 2012. *Statistics for Censored Environmental Data Using Minitab and R*, 2nd Edition, Wiley. ISBN 978-0-470-47988-9

APPENDIX B

Stack Sampling Method Precision Data from ReMAP

As referenced in the main text, a study of stack sampling method precision was conducted under the auspices of the American Society of Mechanical Engineers in 2001²⁹. This appendix is an edited version of a paper presented at the 2017 AWMA/ASME Information Exchange meeting. It provides an overview of the study's results and their implications for assessing emissions.

The ReMAP assessment produced an estimate of the standard deviation of emissions measurements in the form of a power function relationship:

$$S = kC^p$$

where: S = standard deviation
 k = constant determined
 C = concentration
 p = slope of the regression line

A summary of the results of the ReMAP assessment by species is provided in the following table:

Method	Species	Range Used	K	p	95% Confidence for p
US EPA 5	Particulate	15-217 mg	0.0211	1.3063	1.008 – 1.605
US EPA 23	PCDD/F Total	0.5-500 ng	0.1786	0.83	0.594 – 1.066
	PCDD/F ITEQ	0.01-8 ng TEQ	0.1125	0.763	0.411 – 1.115
US EPA 26	HCl	0.1-300 mg	0.1524	0.803	0.708 – 0.898
US EPA 29	Antimony*	1-100 ug	0.188	0.843	-0.001 – 1.687
	Arsenic*	1-100 ug	0.136	1.039	0.692 – 1.383
	Beryllium*	1-100 ug	0.191	0.973	0.244 – 1.702
	Cadmium	1-100 ug	0.978	0.452	0.293 – 0.611
	Chromium*	1-100 ug	0.344	0.833	0.593 – 1.073
	Lead*	50-2000 ug	0.480	0.703	0.577 – 0.929
	Combined *	1-100 ug	0.30	0.821	
	Mercury	5-1000 ug	0.208	0.877	0.643 – 1.112

Using the data in the table above, and the power function relationship, the range of values expected for future single measurements were calculated. The ranges for the two sampling conditions being compared were then examined to see if they overlapped suggesting that significant t-statistics might merely reflect the precision of the method at the levels found in the stack.

²⁹ W. S. Lanier and C. D. Hendrix, "Reference Method Accuracy and Precision (ReMAP): Phase 1 Precision of Manual Stack Emission Measurements," ASME International, 2001.

The Power of Quantifying Reference Method Accuracy and Precision
42nd Annual A&WMA/ASME Information Exchange
John Chandler, A.J. Chandler & Associates Ltd., Toronto, for ASME

INTRODUCTION

In 1996 I led a team that was sampling the emissions from the Pittsfield MWC as part of an ASME Research study. The Department of Energy's National Renewable Energy Laboratory was the principal sponsor. The test was designed to establish the performance of a dry hydrated lime sorbent and powdered activated carbon duct injection air pollution control system retro-fit at an ESP equipped MWC facility. It was anticipated that it would demonstrate achievement of flue gas concentrations at or below the then-promulgated emissions guidelines for small MWCs.

The randomized experimental design was patterned after the design the EPA used to perform the Method 29 validation test on MWCs required by the Clean Air Act.

Sampling was done at the ESP outlet. Actual environmental emissions are further reduced by a downstream wet scrubber.

Given the anticipated low emission profile from the facility, a group of additional sponsors, including Environment Canada, electric utilities, MWCs, and the ASME Research Committee for Industrial and Municipal Waste supported multi-train testing as an add-on to the DOE's project.

Simultaneous, paired data was gathered to determine the precision of Reference Methods 23 (dioxins and semivolatile organics), 26 (halogen hydrides and gases), and 29 (front-half particulates and metals). The four sampling nozzles were arranged in the same vertical plane with the organic samples being collected 3.6 cm apart and the metals samples 5.7 cm apart. The pitot tube was in the center of this array, 8.5 cm distant from the nozzles. All four nozzles were inserted in the stack through a slightly enlarged port and the four sampling boxes were positioned on a dolly that allowed movement into the rectangular duct, and from port to port across the duct.

The data collected at that time became part of the multi-train data that was used for the ReMAP project. Sponsored by the ASME Research Committee on Industrial and Municipal Waste, the Reference Method Accuracy and Precision [ReMAP] Phase 1 study assessed the precision of manual stack emission measurements.

OUTLINE OF ReMAP PROCEDURES

The ReMAP study team reviewed available stack testing data to identify dual or multiple train simultaneous sampling data that could be used to evaluate method precision.

Simply put the ReMAP protocol was to:

- Assess the available data to validate and identify outliers; and
- Utilize the validated data to determine the precision of the methods.

The ReMAP statistical analysis procedure averaged each multi-train test run to provide an estimate of the average concentration for the run (C_i). The standard deviation for the test run (S_i) was also calculated. Clearly, a calculated standard deviation from a single test using a dual sampling probe provides a relatively poor estimate of the true standard deviation of the method at the true concentration. However, after accounting for various biases, a significant array of data from multi-train tests should provide a reasonable basis for estimating the true standard deviation as a function of concentration.

The ReMAP procedure assumed that the standard deviation varied with concentration according to a power function relationship and then testing the fit of the data to that form using regression analysis. This resulted in equations of the form:

$$S = kC^p$$

Where S = standard deviation

C = concentration

k and p are constants from the least squares regression procedure

The regression was completed in the log plane and suitable transformations were employed to address various biases that are created by the transformation process and dealing with different size data sets.

The electronic version of the report can be obtained from ASME if people are interested in the details, but I would simply like to share the results in the form of graphs showing the range of results that might be expected from 99 out of 100 future single measurements *Estimated Value* = $2.567S$ and 99 out of 100 future triplicate tests *Estimated triplicate value* = $2.567 S/\sqrt{3}$ using Methods 5, 23, 26 and 29. These data help to set the scene for discussing the importance of the results.

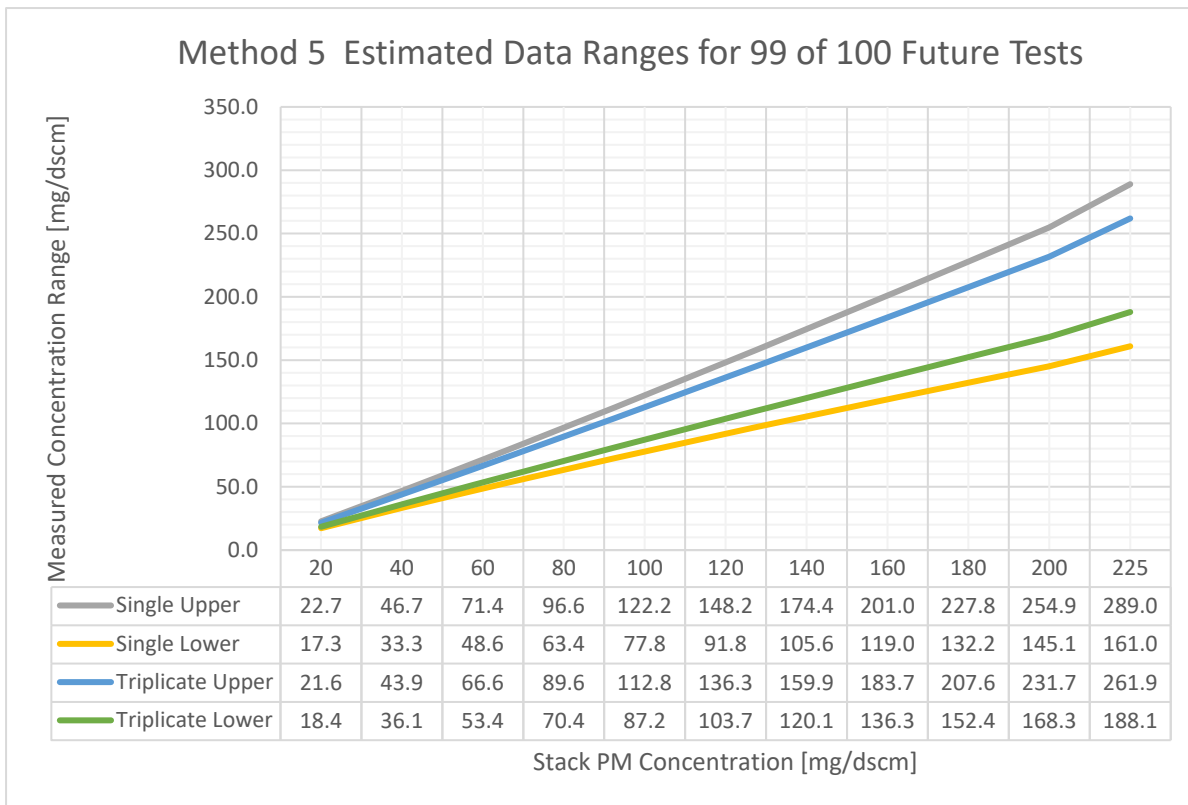
ReMAP RESULTS

Method 5 data included SRI's studies in the early 1970s to validate that Method 5 for the USEPA. Four simultaneous samples were taken at a coal-fired power plant (4 tests) and two MWCs (6 tests and 5 tests). SRI undertook simultaneous sampling at a third MWC with dual trains operating in each of the 4 ports of a round stack. This generated 8 simultaneous measurements over 13 different tests. The Pittsfield data provided 16 dual train Method 5 results.

The data set had a concentration range of 15 to 240 ug/dscm. The ReMAP report cautions that the correlation should not be applied outside this range.

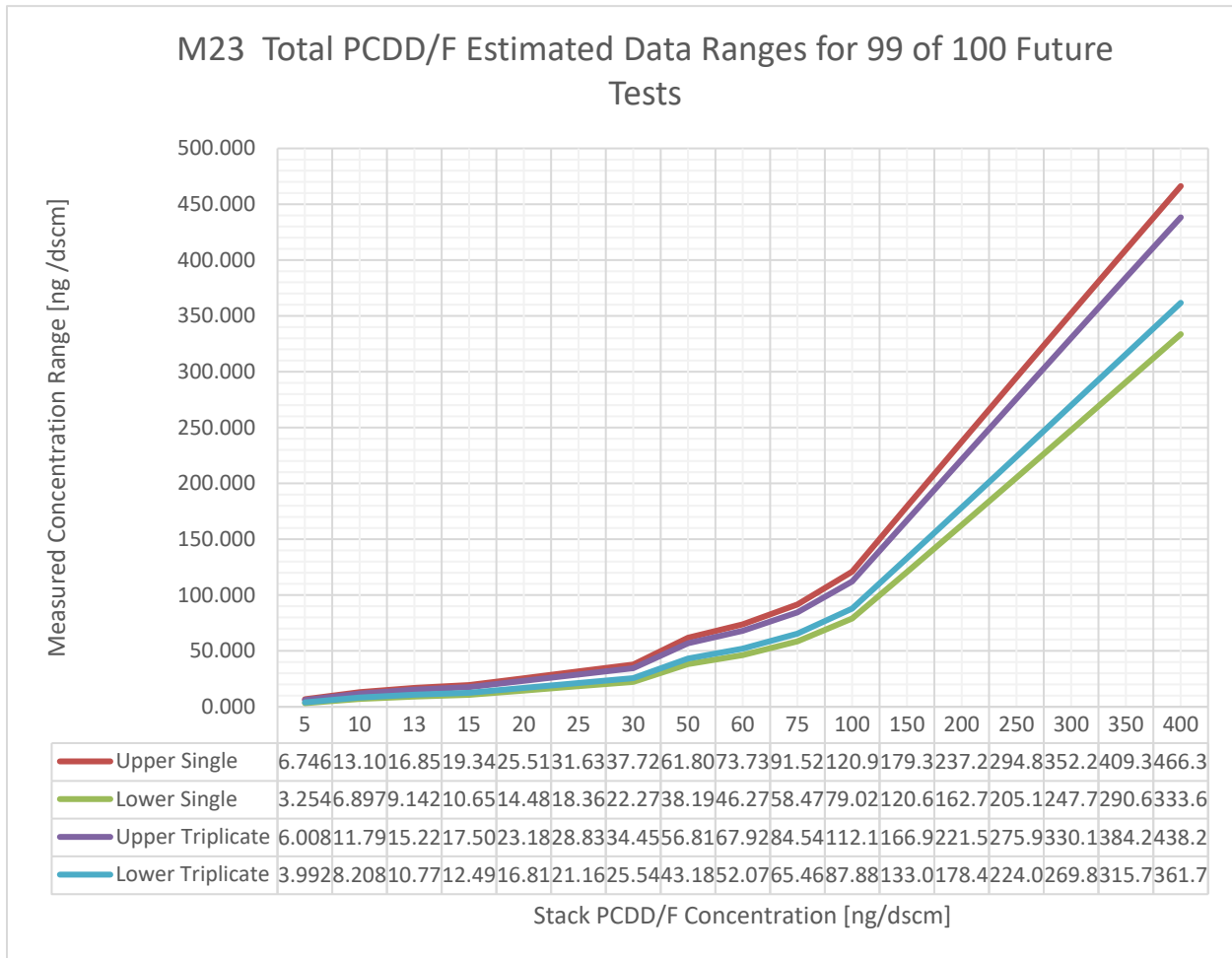
Since newer facilities have concentrations at the low end of this range, it is worth looking at the 20 mg/dscm stack concentration case. The ReMAP result suggests that at this level, 99 of 100 future tests will be within $\pm 13.6\%$ of this value [± 2.71 mg/dscm] and triplicate test results will be within $\pm 7.8\%$ or ± 1.566 mg/dscm. One can extrapolate other points from the plot which shows the measured range for any given average stack concentration, but the curve indicates that the relative standard deviation increases with concentration although not be a large percentage. The ReMAP report suggests that the correlation may have been biased by

the nature of the available data, but without definitive proof of this, all the data were incorporated into the result.



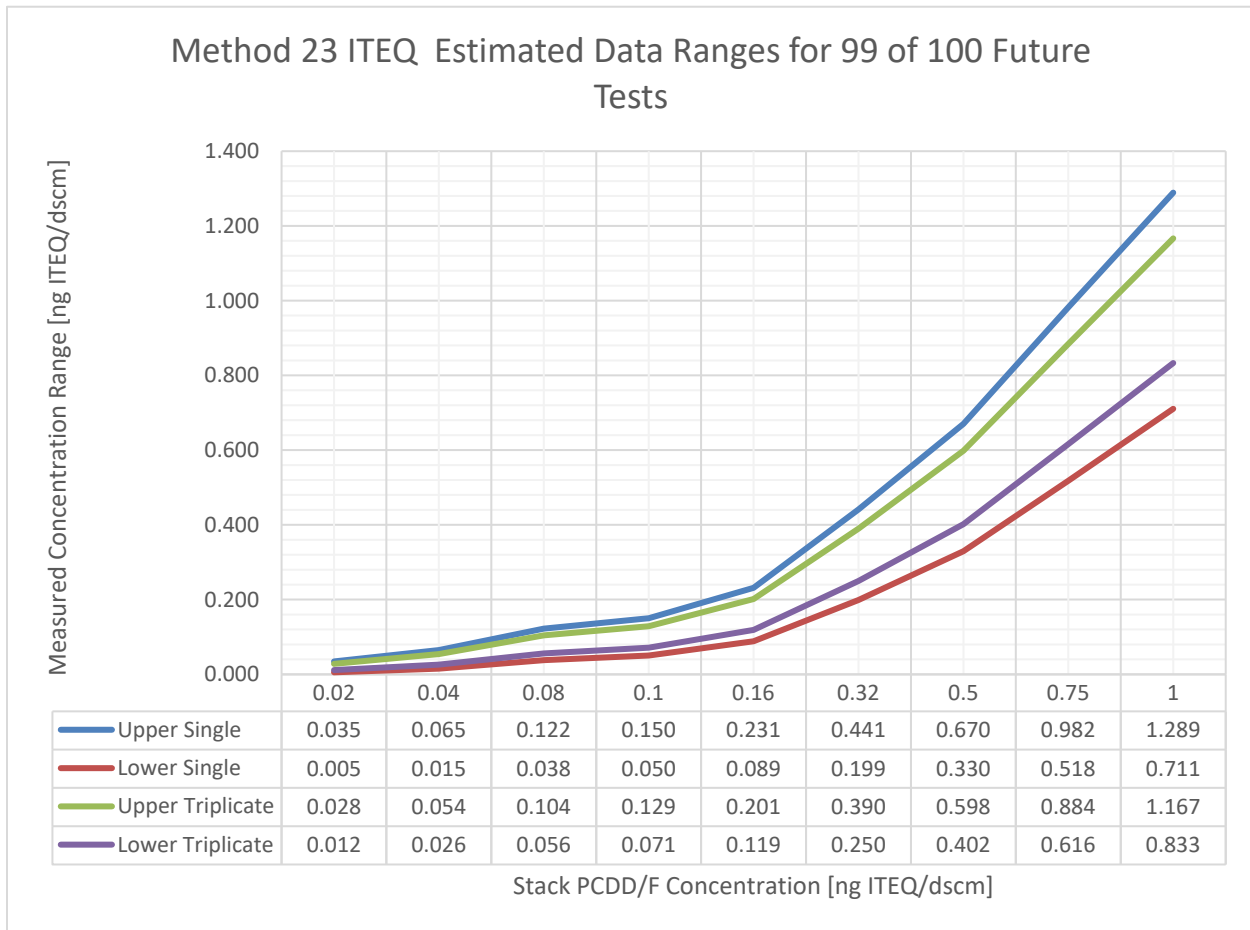
Method 23 dual train data is limited to the Pittsfield data where 19 valid tests were completed, and 3 tests from a light weight aggregate kiln which was simultaneously tested under a US EPA sponsored program by two different sampling contractors. The ReMAP report was issued in 2001 but subsequently the team obtained 5 additional dual train PCDD/F samples from an MWC. While a total of 3 dual train tests were conducted on each of the two stacks at the facility, one sample was lost. These results were at a higher concentration level than the other data and helped improve data quality.

Method 23 PCDD/F – three data sets were used when the 2001 report was amended with the addition of 5 dual train samples from a western MWC. The range of Total PCDD/F concentrations went from 0.7 to 399.82 ng/dscm. Expressed in ITEQ format, the values ranges from 0.020 – 8 ng ITEQ/dscm. The data are presented as two plots, one for Total PCDD/F and the other PCDD/F ITEQ. Unlike the PM data, the RSD reduces as the concentration increases.



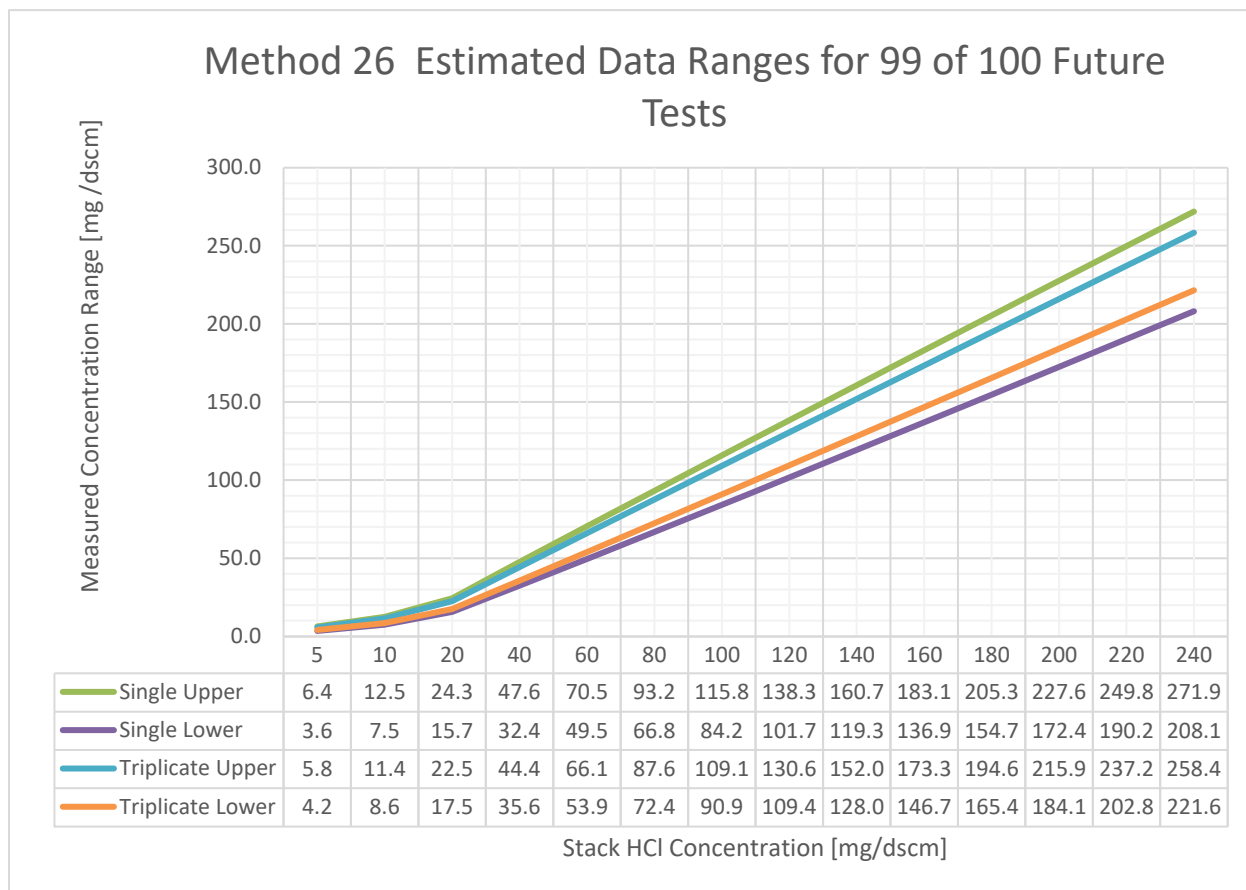
In the US MWC regulations state that the PCDD/F emission rate must be below 13 ng/dscm for new facilities and between 30 and 60 ng/dscm for smaller and older facilities based upon the average of 3 tests. The graph shows that at 13 ng/dscm the triplicate RSD is ±17.1% and at 30 ng/dscm the triplicate RSD is 14.9% reducing to 13.2% at 60 ng/dscm. That suggests that a triplicate average between 52 and 68 ng/dscm would be expected for 99 of 100 future tests, if the facility was in compliance with the 60 ng/dscm total PCDD/F standard. New facilities required to meet the 13 ng total standard would need to have future triplicate results less than 15.2 ng/dscm to comply with the standard.

In Canada, the ITEQ approach is used for the regulatory limit. A value of 0.08 ng ITEQ/dscm is used as the limit. The ITEQ curve shows that at this level, the triplicate RSD is ±30.4% implying that any triplicate result between 0.056 and 0.104 ng/dscm would be considered acceptable.



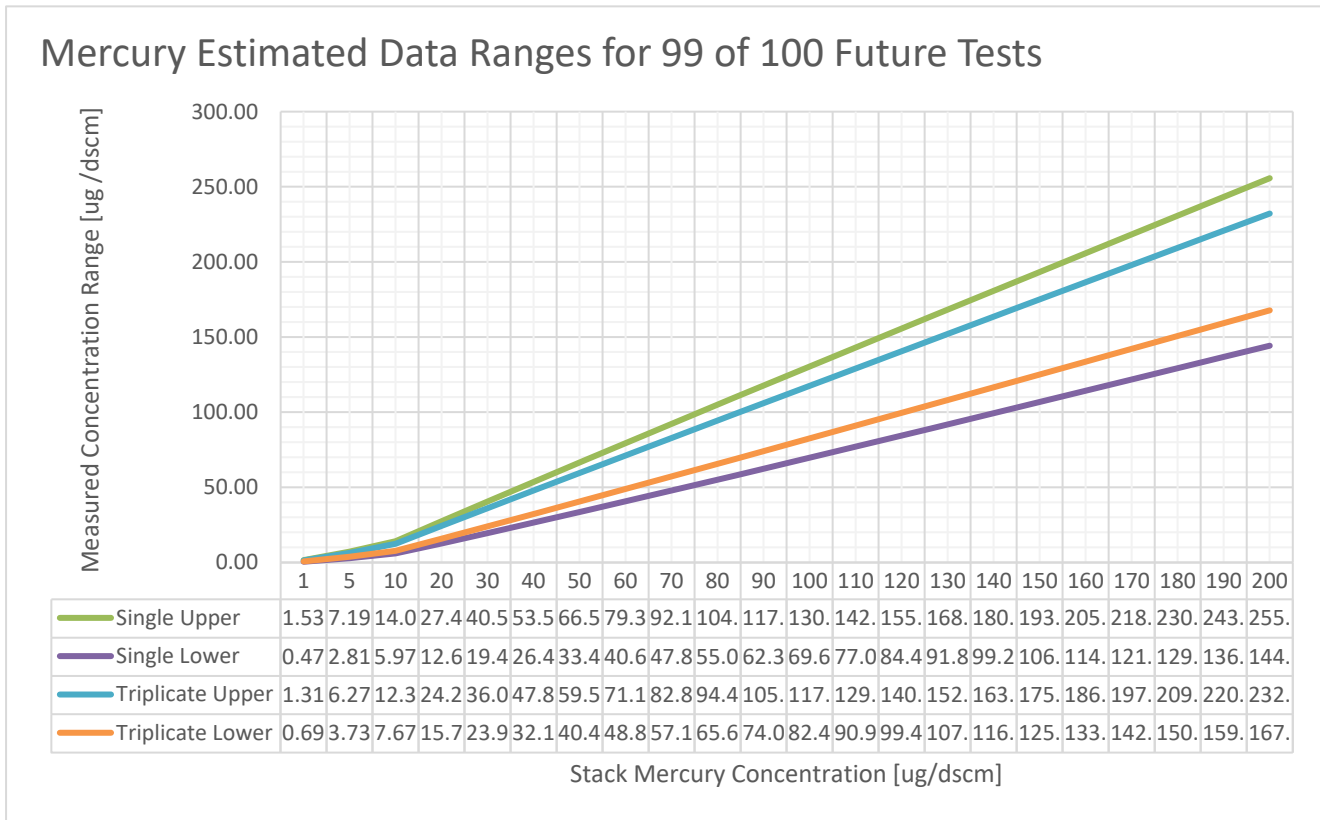
Method 26 multi-train data includes 4 test runs with the quad train at Pittsfield; EPA/OAQPS validation test data collected with both dual (17 tests) and quad (1 test) trains; and, EPA/OSW tests where 9 quad train runs were completed.

Method 26 – HCl ReMAP results were based upon a number of quad and dual train sampling studies which produced average results ranging from 0.19 to 217.3 mg HCl/dscm. The existing MWC standard in the US is approximately 40 mg/dscm and the graph shows that one can expect M26 results at this level to vary by ±11%. The next presentation this afternoon is devoted to HCl testing so I will not discuss this any more.

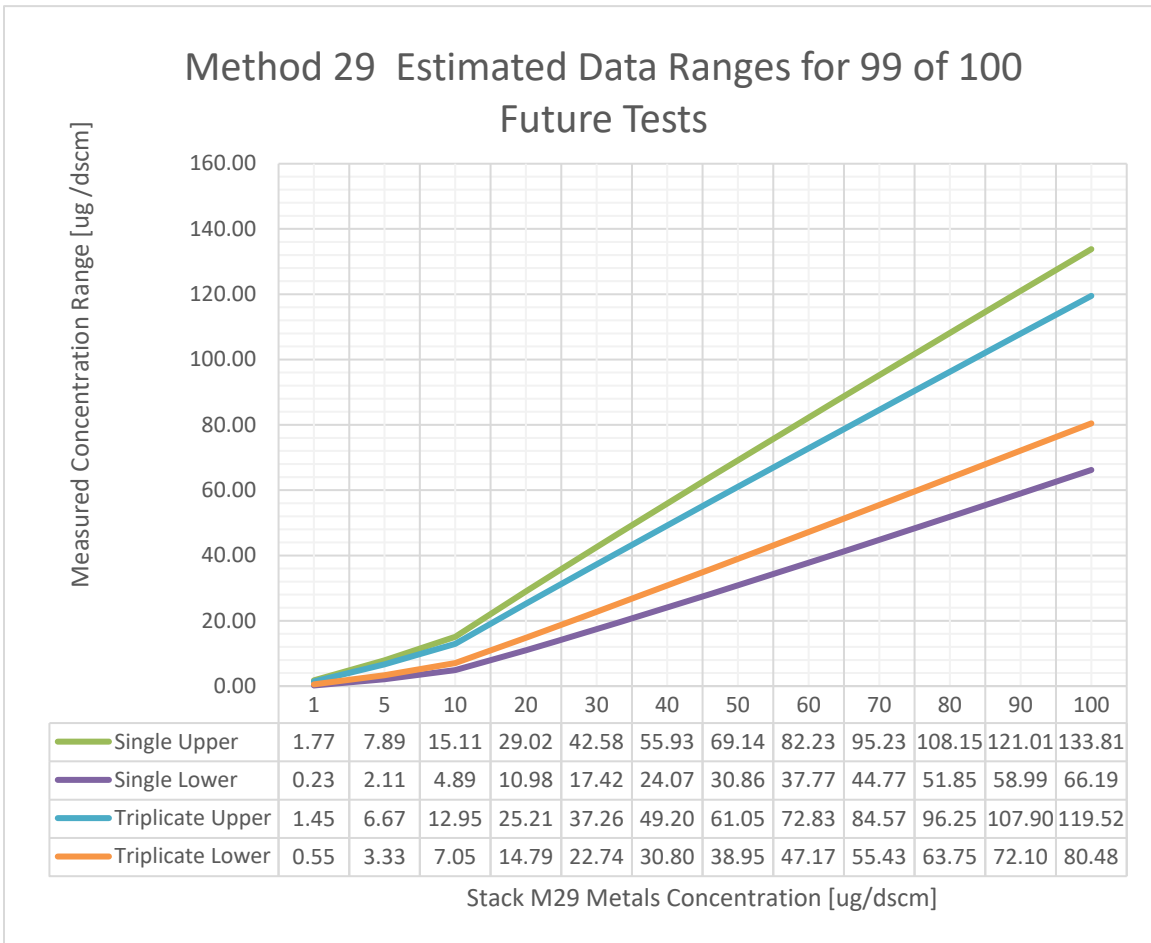


Method 29 data included: EPA/OAQPS validation runs performed at an MWC with quad trains used to complete 8 tests. Method 101b method validation tests conducted at a hazardous waste incinerator included triplicate and dual train data collected with a quad train that was used to compare 101b to Method 29. Pittsfield dual train data provided 16 test results. Dual train data from EPA tests (13 in total) at a west coast MWC were available for mercury only. Tests conducted at the USEPA RTP facility on a pilot scale rotary kiln provided 18 dual train results.

Method 29 – Mercury testing methods that provided data were Method 29 and Method 101. A total of 37 dual train runs were used to establish the correlation. The average concentration 5 to 800 ug/dscm. Over the range to 200 ug/dscm the RSD is relatively constant. At the 50 ug/dscm standard for Large MWC the RSD is 19% and for Small MWC the 80 ug/dscm standard corresponds to an estimated 18% RSD. In Canada where the MWC mercury limit is 20 ug/dscm, the RSD would be 21.4% suggesting that for the facility to be in compliance the triplicate average should be less than 24.3 ug/dscm.



Method 29 – Other Metals are also determined using Method 29. The capture and recovery of samples for analysis is common for 16 specific metals in addition to mercury. These data are regularly required in Canadian jurisdictions. ReMAP addressed antimony, arsenic, beryllium, cadmium, chromium and lead only because these were the species included in regulatory limits at the time. ReMAP analyses showed that Sb, As, Be, Cr and Pb regression results were similar, as would be expected given the sampling process. Combining all the data for these species that was in the range of 1 – 100 ug/dscm provides the composite precision estimate shown in the Metals figure. The results suggest that at concentrations greater than 20 ug/dscm, the results of 99 out of 100 future triplicate tests should deviate by less than 26%. At lower concentrations the deviation rises. The report cautions that at low concentrations, <10 ug/dscm, the imprecision appears to increase asymptotically. While the combined data are convenient, the regression data for each of the metals alone is also provided in the report, and care should be taken when interpreting results based upon the combined curve.



LIMITATION AND USE of the ReMAP RESULTS

How can these results help testing teams, operators and regulators understand sampling results?

Operators who are concerned about their system's performance, may want the added assurance offered by dual train monitoring. If historical data at the facility has been close to the regulatory limit, understanding the variability inherent in the sampling process will help the operator assess the probability that tests might indicate a "failure".

Dual train testing addresses one point that is frequently heard when new research projects are proposed and unknown stack sampling teams are designated to work on the project. The dual train results set a bar for judging the adequacy of the stack testing team's work. Indeed, the authors of the ReMAP work advocated that more dual train sampling be required so that the precision of the work could be assessed. Clearly, if dual train results fell outside the limits suggested by the plots, one might suspect that there were errors or omissions in the procedures that had been followed.

This approach is not any different than that mandated by Method 5i that can be employed on stacks where the particulate emissions are lower than 50 mg/dscm. That method suggests that the minimum precision criteria would be for the RSD for any data pair to be less than 10% as long as the mean PM concentration is greater than 10 mg/dscm. At lower mean PM concentrations a higher RSD is acceptable - at a mean PM concentration of 1 mg/dscm the RSD for paired trains could be 25%. The RSD criteria is then linearly interpolated between 1 and 10 mg/dscm. If the results are outside this range, they are unacceptable for developing a correlation for PM CEMS.

It is instructive to note that the EU standard [EN 1948-5 2015] for assessing the performance of long term PCDD/F samplers suggests that at 100 pg/dscm the difference between the reference method and the long-term method results should be less than 35% and this deviation increases to 100% at 20 pg/dscm.

Clearly, dual train monitoring is more expensive than using a single train. This additional cost needs to be justified but there is also a question of "whether dual train sampling warranted at low emission levels?" A paper published in JAWMA in October 2014 examined this question. One observation that I have made looking at PCDD/F data from 'well controlled' sources is that there is very little difference in the test results. Single train triplicate data were used from 4 annual stack test triplicate results obtained from an ESP equipped long dry kiln cement plant and 17 annual stack test triplicate results from a municipal solid waste (MSW) incinerator before and after the APC system was upgraded from DS/FF to a DS/FF/PAC/SCR configuration. The average annual kiln results for the triplicate tests ranged from 8 – 16 pg ITEQ/dscm whereas the MWC results ranged from 50 – 378 pg ITEQ/dscm before the upgrade and 2.25 – 16 pg ITEQ/dscm after the upgrade. Treating the three tests for any year as though they represent one test period with 3 simultaneous tests, the results were processed in the same manner as the ReMAP approach. The regression lines for each case were plotted and where the regression line for the triplicate annual data crosses the upper confidence limit of the ReMAP regression line denotes the concentration above which the variability is greater than seen from the dual train testing. Below this point there would appear to be little point in considering multi-train testing as little would be added to the precision. For ITEQ values, that occurs at approximately 100 pg/m³.

Note, the 95% confidence intervals of the regression line are mentioned in the preceding paragraph. These curves were developed for the metals and other parameters presented in the ReMAP report. The bounds of the regression line are related to the range of values of the power factor in the standard deviation equation. That is, while the mean value of p was used to develop the curves showing the relationship between stack and measured concentration, there is a statistical case to be made that the p value can vary – between the upper and lower 95% confidence limits.

Knowing the precision of the sampling methods also allows one to assess if changes in fuels or operating conditions have affected the emissions from a source. For instance, as the cement industry looks to employ alternative low carbon fuels [ALCF], citizens around their facilities question whether they are being exposed to greater emissions. The concerns are heightened when a facility proposes burning components of the MSW stream. By monitoring emissions during periods when the ALCF is burned and comparing those to emissions created when the kiln is fired with coal or petcoke it is possible to establish if emissions change.

While statistical tests can indicate if the hypothesis that mean values of two different sample groups are the same is likely to be correct, it is often easier to create a boxplot of the data and see if the interquartile range of the data overlap. The boxplots comparing stack emission data are best done with the log transformed data given that emission data is typically log normally distributed. Boxplots have been used to quickly identify if changes in ALCF influenced stack emissions at one facility in Canada.

Those boxplots for mercury showed that the boxes overlapped suggesting that there is no change in emissions between the baseline fuel and the use of ALCF. Note, there are two LCF tests since it was necessary to sample in two areas of the ESP discharge duct due to its size. The lack of any shift in emissions should not be surprising as the ALCF used was non-recyclable plastics and rubber and tire fluff, none of which would be anticipated to contain mercury.

On the other hand, the boxplots for chromium showed that there were some differences between the samples, both between the A and B sides of the LCF testing, and between those tests and the baseline testing. The question becomes, is that difference significant or is it merely the type of variability that we might expect given the precision of the test method? To address that question, it is necessary to take a closer look at the precision data derived in the ReMAP program with the aid of the diagram on the next page.

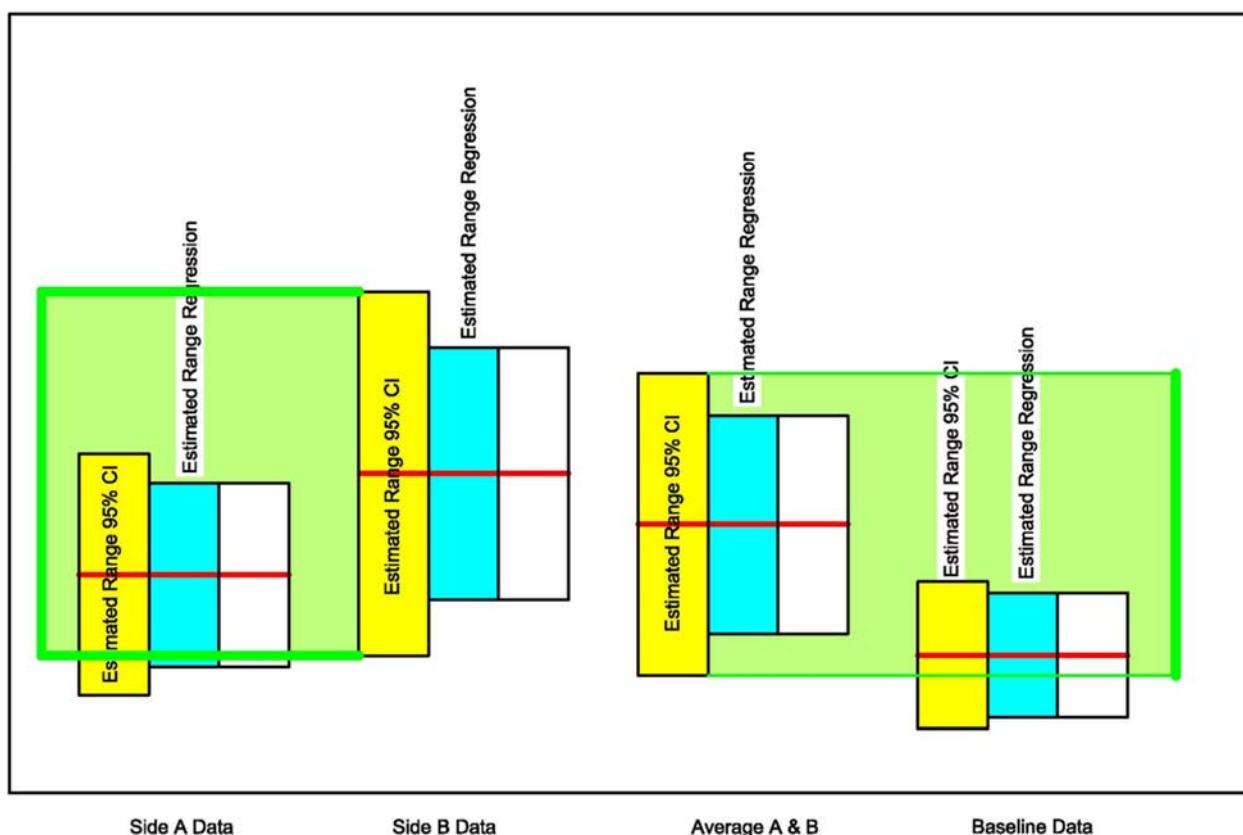
Using the average of the Cr test data for each of the alternatives shown in the boxplot, we obtain:

- Baseline – 1.9713 ug/dscm;
- Test A – 3.1241 ug/dscm;
- Test B – 4.5760 ug/dscm; and
- combined Test A and Test b – 3.85 ug/dscm.

If we use the standard deviation from the regression line for the 5 metals and calculate the upper and lower bound of 99 out of 100 future triplicates, the Average of Location A and B results are not captured within the range of the data. However, if we used the 95% UCL for p for Cr, the two test locations produce data that is similar, suggesting that the differences are within the precision of the method. This lets us combine the stack

data from the two locations during the ALCF testing and compare the resulting average for the exit concentration of these locations to the triplicate for the Baseline testing.

Again, the bounds generated for the triplicate baseline data and the triplicate average ALCF test values using the p value for the combined metals do not compare well. However, by using the upper confidence interval of p for the Cr data the averages for both the tests are in the same range. While the upper confidence limit of p was used, since the regression takes into account all the data, we can conclude that the variation is the result of the imprecision of the sampling method.



These techniques have been used to investigate differences in emission concentrations between Baseline runs conducted biannually since 2010 and three different types of ALCF fuel blends. Typically, the variations have been covered by the standard deviation calculated from the best estimate of the regression line. There has not been a need to examine the impact of the confidence intervals of the regression line to show that the differences identified were within the range of the imprecision of the method.

EXTENDING ReMAP DETERMINATIONS

The biggest limitation to the ReMAP data is the paucity of data available. Not only is the data limited, but there are only a limited number of tests. Most of the regression lines were determined from as few as 27 dual train tests for PCDD/F; 31 for HCl; 34 tests for Sb, and As; 42 tests for Cd, and Pb; 44 tests for PM; and 73 tests for Hg. The greater the number of data points the better the fit of the regression curve.

The second limitation is the range of concentrations represented by the data. The wider the range the better. Since 2000 it has been observed that lower emission concentrations have become the norm, and there is a need to get more data at the lower end of the concentration ranges.

Lower stack concentrations also result in the occurrence of less than detection limit results when laboratory analyses are completed. These data are of limited use in attempting to establish the precision of the methods at lower concentrations. This suggests that longer sampling times should be the norm if low concentration stacks are being tested. Longer testing can alter the variability of the results and this needs to be taken into account in any evaluation.

One area where the BDL values are not as restrictive is when determining the ITEQ values for PCDD/F tests. The 2014 JAWMA paper that I discussed earlier employed the Kaplan Meier approach suggested by Helsel. This is frequently used in survival analysis for computing the mean of right-hand censored data. Essentially the procedure generates the mean of the congener values times their respective TEFs. When the mean calculated by this process is multiplied by 17 it provides a good estimate of mean TEQ value. That was used for comparing data from the MWC with the robust APC system because even with 4 hour sample times, BDL values were encountered for some congeners.

Of course, the list of species that have been examined is limited. While the Pittsfield testing generated dual train metals data for 26 elements from 16 paired tests, without any other similar data, it was decided to restrict the ReMAP analyses to elements with multiple tests series. There is a need for more elements to be included in such analyses. After all, Method 29 lists 17 metals that can be assessed. At least these elements should be evaluated.