Development of Emission Factors for Pulp and Paper Mill Sources

John E. Pinkerton
NCASI
P.O. Box 13318
Research Triangle Park, NC 27709-3318
jpinkerton@ncasi.org

Arun V. Someshwar, David Word
NCASI Southern Regional Center
402 SW 140th Terrace
Newberry, FL 32669-3000
asomeshwar@src-ncasi.org, dword@src-ncasi.org

ABSTRACT

NCASI has developed emission factor information for pulp and paper mill sources from a large body of emission test data. This information is widely used by NCASI member companies for air permitting, emission inventories, and annual chemical release reporting. In this paper, the procedures used to review stack sampling test reports, identify key factors affecting emissions, process test data, and perform statistical analyses are described. Techniques for handling data sets with measurements below method detection limits and with potential outliers are discussed. The summary and background information for each emission data set that is made available to prospective users is enumerated.

INTRODUCTION

Over the past twenty years, a significant amount of emission testing has been done at pulp and paper mills with collective costs well in excess of $10 million. In addition to major industry-supported multi-mill sampling efforts associated with development of MACT emission standards for pulp and paper mill sources in the U.S. and with sector- specific regulations in Canada, considerable testing has been done at individual mills to meet permitting requirements, respond to state and local regulatory programs, and to better understand operating and process variables affecting emission rates of certain pollutants. Although all of this sampling was not done to generate emission factors for pulp and paper mill sources, it represents a large body of data that can be exploited for that purpose.

In this paper, the procedures used by NCASI to develop emission factors from the available sampling data are described. The procedures address situations that arise when processing data obtained with different sampling methods with varying method detection limits, from unit process operations with multiple emission points, or from similar equipment but with different control systems or operating characteristics. The procedures define how to treat results that are below method detection limits and results that are apparent outliers. Calculation methods for obtaining means, medians and other central tendency measures for data sets that may be modestly to highly censored are outlined.

EMISSION FACTOR DEVELOPMENT

Sampling Report Review

Following a sampling event, the testing firm or organization prepares a summary report with the results and descriptions of the test methods employed, sampling locations, and calculation procedures. Appendices normally contain raw sampling data, process operating data, emission rate calculations, off-site laboratory analyses, QA/QC documentation, etc. A draft of the test report is typically reviewed by mill and/or corporate staff to ensure accuracy of process information, adherence to mill permit and state/local agency requirements for sampling, and consistency with any prior test results on the same sources (or identification of reasons for major differences). Final reports are then provided to the appropriate regulatory agencies for their review and approval.

Test reports obtained by NCASI that are considered for use in developing emission factors undergo an initial evaluation to determine their acceptability. Reports without sufficient process and production information for computing an emission factor in the desired units are rejected unless the mill can provide this information for the period of emission testing.

When the necessary process and production information is available, the following items are then considered:

- Test methods employed
- Method detection and quantitation limits
- Representativeness of vents tested on a process unit with multiple vents
- Any conditions noted in the report indicating sampling problems, abnormal operating conditions, or process upsets
- Run-to-run consistency

More detailed reviews of calculations, QA/QC results, laboratory data, etc. are generally only done when results appear to be questionable.

When apparent problems are identified, additional clarification may be sought by contacting the testing firm or mill staff. In many cases, errors in calculations or transcription mistakes can be fixed or missing information provided.

The outcome of the sampling report review may be complete acceptance, total rejection, rejection of one or more individual sampling runs for a given pollutant, or rejection of all results for one or more pollutants.

Method Detection Limit Considerations

Stack sampling data judged to be of acceptable quality and completeness are further processed for the purposes of emission factor development. A fairly common occurrence, especially for gaseous organic compounds and trace metals, is the concentration for a given substance on one or more sampling runs is reported as “less than the method detection limit” or “non-detect”. The method detection limit may not be the same for each sampling run because of variations in sampling rates and lengths of sampling runs. Furthermore, different sampling methods for the same substance may have been employed which have significantly different method detection limits. In order to calculate emission factors, some value must be assigned to each non-detect. Three options are zero, one-half the method detection limit, and the method detection limit.

For a unit process with only one stack or vent, NCASI assigns one-half the method detection limit for each sampling run where a value was reported as non-detect. Since method detection limits are

typically given in concentrations (ppm for gases and gr/dscf for particulate matter), this value is first converted to an emission factor and then one-half of the emission factor value is used. Although it could be argued that it would be more appropriate to assign a zero value to a non-detect if there is no reason to expect the substance would be present in stack or vent gas, it is difficult to prove a substance could not be present in extremely low concentrations. If all sampling runs in an emission test are reported as non-detect for a substance, then a value of one-half the detection limit for the run with the lowest detection limit is used as the emission test average. If one or more sampling runs gives values above the method detection limit, then the emission test average is calculated using one-half the method detection limit for each sampling run reported as non-detect.

For process units with multiple vents, the procedure described in the preceding paragraph is followed for individual vents where non-detect values have been reported on one or more sampling runs. The emission factor for the process unit is obtained by summing the factors for the individual vents. Unless all sampling runs on all vents are non-detect, the total is considered as a "detect" value. It is recognized this procedure may give an unrealistically high total in the situation where a process unit consists of vents with both high and low flow rates, and the only "detect" values are for the low flow vents. Alternatives are being examined to better handle this situation.

When all sampling runs in an emission test yield non-detect values for a substance, the test result is flagged because it may need to be treated differently in the emission factor calculations that follow.

Grouping of Emission Tests

Emission tests are initially grouped by process units such as paper machines, boilers, kraft recovery furnaces, smelt dissolving tanks, lime kilns, brown stock washer systems, bleach plants, oxygen delignification systems, thermal oxidizers, etc. For each type of process unit, further subdivisions are made for the purposes of calculating emission factors. Such subdivisions may be based on equipment types, fuel types, furnish types, wood species, control devices, process operating conditions, or any other factors known to affect emissions. Since different variables can be important for different pollutants, the subdivisions for a unit process are pollutant-dependent.

The creation of subdivisions requires process knowledge and engineering judgment. While logical subdivisions of emissions data for a unit process can be obvious in many cases, such as separating metals emission data according to type of particulate control device and fuel burned, others may only be apparent after careful analysis of emission test results. For example, NO_x emissions from lime kilns have been found to be related to type of fuel burned (natural gas, fuel oil, petroleum coke) and whether or not steam stripper off-gases, which contain ammonia and reduced sulfur compounds, are sent to the lime kiln to oxidize the reduced sulfur compounds. As additional test data become available, there is a need to reevaluate the existing subdivisions and perhaps modify them or create new ones.

In situations where process knowledge and engineering judgment are not sufficient to determine if subdivisions should be made for a given pollutant, some type of statistical testing could be employed[1], e.g. a Student t-test to compare data segregated into two subdivisions. Of course, use of statistical tests involves many additional decisions – what should be the level of significance, how to treat non-detects, whether the data are or are not normally distributed, whether to use individual sample runs or the averages for an emission test, minimum number of tests needed to make a meaningful statistical comparison, etc. To date, NCASI has not used statistical approaches to create subdivisions.

Calculation Procedures

The group of emission tests for a particular pollutant, unit process, and unit process subdivision constitute an emission data set. The data set will consist of one or more emission tests on one or more

emission units. An emission test represents the average emission rate determined from two or more individual runs on the same source under relatively steady operating conditions over a period ranging from a few hours to a few days. Some emission units may have been sampled on multiple occasions. When more than one emission test has been conducted on an emissions unit under similar conditions, an average value for that emissions unit is obtained by averaging all the emission tests. In calculating the average for an emissions unit, non-detect values that have been assigned one-half the method detection limit are treated as if they are "real" values. When all sampling runs on an emissions unit are non-detect, this fact is noted since it will affect subsequent emission factor calculations.

The emission data set used for calculation of emission factors is comprised of single average values for one or more individual emission units. The single value may represent one or more emission tests. Thus, a value for an emissions unit with four emission tests is given the same weight as a value for a unit that has only been tested once.

The next step in the procedure is to remove the average for any emission unit if it has (1) been flagged as "non-detect", i.e. all sampling runs for this compound on the emission unit were below method detection limits, and (2) the method detection limit is more than two times the highest "detect" emission unit average in the emission data set. This step is necessary because emission data sets sometimes contain sampling data obtained with different testing methods that have significantly different detection limits. Inclusion of a non-detect based on a method with a high detection limit and treating the assigned value of one-half the method detection limit as a "real" value is not reasonable.

Emission data sets are then examined for the presence of emission unit averages that are suspiciously low or high compared to the others in the data sets. Statistical tests may be applied to data sets to help identify such outliers[1]. When the data set has 25 or fewer values above detection limits, Dixon's Extreme Value Test is used. Rosner's Test is applied to data sets with over 25 values above detection limits. For these tests to be valid, the values remaining after removal of a suspected outlier must be normally distributed. If an extreme value is suspected to be an outlier, additional review of the emission unit characteristics, operating conditions during the emission test, sampling methodology, QA/QC information, etc. is conducted to determine if it should be deleted from the data set.

Once outliers have been removed, the mean and median of the data set are calculated. The procedure used depends on the percentage of non-detects in the data set. The calculation is straightforward when non-detects represent 15% or less of the data. When data set has 15 to 50% non-detect values, the median is still computed using all the values but a 15% trimmed mean is computed for data sets with 7 or more values. The 15% trimmed mean discards the lowest 15% and highest 15% of the data points before the mean is computed. For example, if a data set has 20 points, the lowest 3 and highest 3 points will not be used in the mean calculation. When the data set contains over 50% non-detect values, more involved statistical procedures described by Hinton[2,3] have been applied to obtain a measure of central tendency for the data set. However, NCASI is currently evaluating other options for dealing with data sets containing more than 15% non-detects, including techniques described by Helsel[4]. Lastly, if all emission units in the data set have non-detect values, i.e. 100% non-detects, no mean or median is calculated and the lowest method detection limit for any of the units is noted.

Emission Factor Information for Users

For each emission data set, the following summary information is currently reported:

- Number of emission units
- Number of emission units with only non-detects
- Mean or trimmed mean (for data sets with 50% or less non-detects)
- Median (for data sets with 50% or less non-detects)

- Central tendency (for data sets with over 50% non-detects)
- Lowest and highest individual unit averages

Individual emission unit data comprising the data set are also provided in tabular form, including data that were eliminated from the emission factor calculation due to either high detection limits or outlier considerations. The individual emission unit information consists of the following:

- Emission unit and control equipment description
- Operating information relevant to the emitted pollutant
- Test method
- Year(s) of emission testing
- Range for individual sampling runs
- Average emission rate

Emission factors developed by NCASI for the most common pulp and paper mill sources are based on the following production units (per hour):

- Tons black liquor solids processed - kraft recovery furnaces, smelt dissolving tanks, black liquor oxidation systems
- Tons lime produced – lime kilns, calciners, lime slakers, causticizers
- Tons pulp produced – digesters, evaporators, thermal oxidizers, brown stock washer systems, oxygen delignification systems, knotters, deckers, bleach plants, mechanical pulping systems, repulping and deinking systems
- Tons (air dried finished tons) produced – paper machines, pulp dryers
- Million Btu heat input – boilers

All of this information is compiled and maintained in Microsoft Excel® databases. Periodic summary reports are published by NCASI. The most recent are *Compilation of Speciated Reduced Sulfur Compound and Total Reduced Sulfur Emissions Data for Kraft Mill Sources*[5]; *Air Toxic' and Total Hydrocarbon Emissions Data for Sources at Kraft, Sulfite and Non-Chemical Pulp Mills – An Update*[6]; and *Compilation of Criteria Air Pollutant Emissions Data for Sources at Pulp and Paper Mills Including Boilers*[7]. These reports will be updated in early 2009 after data from a 20-mill emissions sampling program conducted in Canada[8] and additional mill-provided test data are incorporated in the data base. The update will also incorporate revised procedures for handling emission data sets containing more than 15% non-detects.

Emission factor information developed by NCASI is widely used by the North American pulp and paper industry for annual chemical release reporting under the U.S. Toxics Release Inventory (TRI) and Canadian National Pollutant Release Inventory (NPRI), air quality permitting, and state/provincial/local agency emissions inventory submissions. Because users have access to much more information than a single value representing the mean of an emissions data set, they have the ability to review all of the available data and determine what the most appropriate factor is for their particular circumstances. For example, if an emission limit must be proposed in a permit application for a new emission unit, use of the mean or median value of an emission data set comprised of sampling results from similar units would not be appropriate. In this situation, the user could review the individual unit test results in the emission data set to come up with a more reasonable number, e.g. the highest observed value or the mean plus two standard deviations. On the other hand, the mean or median value would be a logical choice to estimate emissions for an annual inventory report.

Similarities and Differences from the AP-42 Process

The starting point for both the NCASI and AP-42[9] procedures is collection and review of stack sampling data. It is essential that reviews be conducted by individuals familiar with the process units

being sampled and stack testing methods. Qualified reviewers would presumably come to similar judgments regarding the acceptability of the data generated in large multi-mill sampling programs as well as those contained in mill-provided sampling reports. Unlike AP-42, NCASI does not assign a quality rating to emission tests.

For AP-42 purposes, non-detects are always assigned a value of one-half the method detection limit and this value is used in all calculations. NCASI will not include an emission test where all sampling runs are reported as non-detect and the method detection limit is greater than twice the highest reported "detect" value in an emissions data set for a given pollutant and process unit.

Similar to NCASI, emissions data for AP-42 is grouped according to process unit type with further subgrouping as necessary to account for other factors that have a significant impact on emissions of a pollutant. In general, it would be anticipated that different analysts with equivalent levels of process knowledge would arrive at the same subgroupings for emissions data from the same process unit type. NCASI has not used any form of statistical testing for subgrouping decisions; it is not known to what extent statistical tools have been used in preparing various AP-42 sections.

In the AP-42 publication, emission factors are generally presented as a single value which is the mean of the emissions data set, with non-detects included at one-half the method detection limit. A quality rating (A, B, C, D, or E) is assigned to each factor. Statistical tests are not used to identify possible outliers. A description of how factors for the emission unit were developed is usually available in a background information document covering types of emission units found in an industrial source category or subcategory, e.g. chemical wood pulping. These documents may or may not contain summaries of emission test data used to compute the average emission factor.

With respect to current AP-42 coverage of pulp and paper emission sources, the emission factors in Section 10.2, Chemical Wood Pulping, largely reflect emission testing done in the 1970s. There are placeholders for sections on pulp bleaching and papermaking. The electronic WebFIRE data base has a very limited amount of newer test information for some pulp and paper mill sources, but the most recent test reports are circa 1990. Emission factors for industrial boilers are in Chapter 1, and are reasonably up-to-date.

SUMMARY

The procedure used by NCASI to process stack sampling data and develop emission factor information for pulp and paper mill emission sources has been described. The initial, and most important, step in the procedure is thorough review of sampling reports by individuals who are familiar both with the sampling methods employed and the process units tested. How non-detect values, potential outliers, multiple tests on the same emissions unit, and emission data sets with considerable numbers of non-detect values are handled has been discussed. Similarities and differences between the approaches used by NCASI and those used for AP-42 emission factor development, and between the amount of information made available to potential users of the emission factors, have been enumerated.

The emission factor information developed by NCASI has been widely used by North American pulp and paper mills for permitting, inventories, and TRI/NPRI reporting. Since the underlying emissions data for each factor are readily available, users are not limited to using a single value such as a mean or median as the best estimate for their particular unit and desired use of the value (permitting versus inventory reporting, for example). The database assembled by NCASI is comprehensive in coverage, reasonably up-to-date, and comprised of carefully reviewed sampling information.

REFERENCES

1. EPA. Data Quality Assessment: Statistical Methods for Practitioners. U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC. EPA AQ/G-9S. 2006.

2. Hinton, S.W. *Estimating the Mean of Data Sets that Include Measurements below the Limit of Detection.* NCASI, Research Triangle Park, NC, 1991; NCASI Technical Bulletin 621.

3. Hinton, S.W. "Statistical Procedures for Addressing Non-Detect Results in Environmental Analyses". *TAPPI Journal* **77** (4): 83. 1994.

4. Helsel, D.R. *Nondetects and Data Analysis: Statistics for Censored Environmental Data*. Wiley; New York, NY. 2005.

5. Someshwar, A.V. *Compilation of Speciated Reduced Sulfur Compound and Total Reduced Sulfur Emissions Data for Kraft Mill Sources.* NCASI, Research Triangle Park, NC, 2002; NCASI Technical Bulletin 849.

6. Someshwar, A.V. *Air Toxic' and Total Hydrocarbon Emissions Data for Sources at Kraft, Sulfite and Non-Chemical Pulp Mills – An Update.* NCASI, Research Triangle Park, NC, 2003; NCASI Technical Bulletin 858.

7. Someshwar, A.V. *Compilation of Criteria Air Pollutant Emissions Data for Sources at Pulp and Paper Mills Including Boilers.* NCASI, Research Triangle Park, NC, 2004; NCASI Technical Bulletin 884.

8. Jacques Whitford Environment Ltd. *Report on the Pulp and Paper Study on Air Quality*. Prepared for the Forest Products Association of Canada, 2003.

9. EPA. *Compilation of air pollution emission factors. Volume I: Stationary point and area sources* (5^{th} edition). AP-42. : U. S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. 1995.

KEYWORDS

Emission Factors
Kraft process
Pulp mills
Paper mills