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Time-Variability of NO_x Emissions from Portland Cement Kilns

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Due to the presence of autocorrelation between sequentially measured nitrogen oxide (NO_x) concentrations in stack gas from portland cement kilns, the determination of the average emission rates and the uncertainty of the average has been improperly calculated by the industry and regulatory agencies. Documentation of permit compliance, establishment of permit levels, and the development and testing of control techniques for reducing NO_x emissions at specific cement plants requires accurate and precise statistical estimates of parameters such as means, standard deviations, and variances. Usual statistical formulas such as for the variance of the sample mean only apply if sequential measurements of NO_x emissions are independent. Significant autocorrelation of NO_x emission measurements revealed that NO_x concentration values measured by continuous emission monitors are not independent but can be represented by an autoregressive, moving average (ARMA) time series. Three orders of time-variability of NO_x emission rates were determined from examination of continuous emission measurements from several cement kilns. Long-term variations are related to changes in process control, feed composition, fuel composition, and types of product produced and are reflected by nonperiodic drift in the time series. Intermediate-term variations result from changes in process control and operator technique. Very short-term variations, which are not normally visible due to the averaging process applied to data collection, are related to the dynamics of the flame. Autocorrelation effects within the emission rates extend over a period of 8−10 h. The high levels of autocorrelation observed between sequential readings result in underestimating the variance of the average emission rate unless autocorrelation effects are considered. Although thousands of NO_x measurements may be recorded, autocorrelation of sequential measurements implies that many of them are redundant.

Introduction

NO_x formation during the pyro-processing of raw materials is dependent upon many independent process variables whose values vary at each portland cement kiln. Consequently, statistical parameters associated with NO_x concentration in stack gases are kiln specific. Because of the multivariate nature of the independent variables affecting NO_x concentrations, a large number of measurements are required to make accurate estimates of NO_x statistical parameters. Specific information about the diversity of manufacturing systems and legion of independent variables is contained in (*1*).

Until the enactment of the 1990 Amendments to the Clean Air Act by the US Congress, concern for the reduction of NO_x emissions from portland cement plants was essentially limited to California. Since the enactment, many states, and especially those located in the Northeastern Ozone Transport Region, have conducted reasonably available control technologies (RACT) analyses for NO_x reduction. On November 7, 1997, the United States Environmental Protection Agency (USEPA) proposed in the *Federal Register* (*2*) a rule that requires up to 70% reduction of mass emissions of NO_x from portland cement kilns (SIP Call). This rule would apply to portland cement plants in 22 states (*3*) that participated in the Ozone Transport Assessment Group. A NO_x trading plan was proposed (*4*) which would allow plants to buy and sell emission credits (*5*) in a manner similar to the acid rain trading program affecting the sulfur dioxide standards. Whatever items are included in the final EPA rule, accurate measurements of NO_x emission rates will be required by individual portland cement plants.

Although the SIP Call and the regulatory requirements in California and the recent RACT analyses in states such as Maine, Maryland, and Pennsylvania have produced some useful information and data regarding NO_x generation and reduction in the portland cement industry, the statistical analyses of NO_x in cement kiln stack gases have not been rigorous. Correct calculation procedures for statistical parameter estimates such as means and standard deviations must be used. Such statistics are essential for the comparison of NO_x emissions before and after application of alternative control techniques to determine their effectiveness for NO_x reduction. A mandatory prerequisite for the determination of the technical feasibility and applicability of control techniques for individual plants and the portland cement industry affected by requirements similar to the USEPA's recent SIP Call is knowledge of the true average emissions and the variability associated with these emissions.

The authors of this paper have conducted numerous such investigations in the portland cement industry. The significant results of these studies are presented below.

Characteristics of NO_x Emissions from Kiln Systems

NO_x emissions from portland cement kilns are inherently variable. Evaluation of process modifications requires the application of statistical analyses to data obtained from continuous emission monitors (CEMs) which record measurements of NO_x at closely spaced time intervals. These measurements are accumulated and averaged by a process control computer at preset time intervals. Thus, the available data for a cement kiln may be a 30-s average, 1-min average, 6-min average, 30-min average, or 1-h average. All of these time intervals have been represented in data from the various cement kilns studied.

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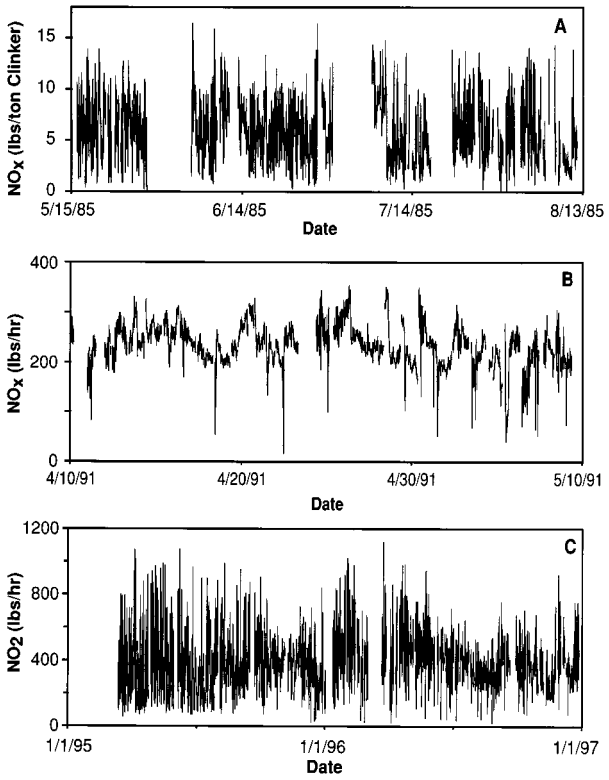

FIGURE 1. (a) NO_x emission measurements (13 561 6-min average) for the Crestmore plant of Riverside Cement Company which were included in the response to Rule 1112 of the South Coast Air Quality Management District (*6*); NO_x emission measurements (5436) for the Maryneal plant of Lone Star Industries Company which were included in the air permit application to the TACB (*7*); and (c) NO_x emission measurements (11 736) for the Thomaston plant of Dragon Products Company which were included in their air permit application submitted to the Maine Board of Environmental Protection (*8*).

Normally, NO_x emissions are calculated in terms of NO_2 although NO is the dominant nitrogen oxide present (*1*). The amount of NO_x in gaseous emissions from portland cement kilns have been presented in terms of several units such as pounds of NO_2/h, parts per million, or normalized to the product output (pounds of NO_2/ton of clinker). Generally, the units of measurement are set by the regulatory agency that receives the emission report or has jurisdiction for the air emission permit.

The high variability of measurements of NO_x emissions from the portland cement pyro-process (Figure 1a−c) is common to all plants investigated. NO_x emission data (*6*−*8*) for three kilns are shown in Figure 1a−c. The Crestmore plant owned by Riverside Cement Company and located in Rubidoux, CA manufactured cement clinker using the long-dry process. The Maryneal plant owned by Lone Star Industries, Inc. and located in Maryneal, TX manufactures cement clinker using a Krupp-Polysius preheater process. The Thomaston plant owned by Dragon Products Company and located in Thomaston, ME uses the wet process. Dragon installed a Pillard Rotoflam burner system with indirect coal firing in February, 1995 prior to collection of the data shown in Figure 1c.

Although, these kilns use different pyro-processing systems, they all demonstrate variable NO_x emissions. The data for the Crestmore and Maryneal plants (Figure 1a,b) are 6-min averages of the CEM measurements. One-h averages are shown for the Thomaston plant (Figure 1c). Examination of these data, which represent time series, reveals three orders of variation. The observed data consists of long-term trends

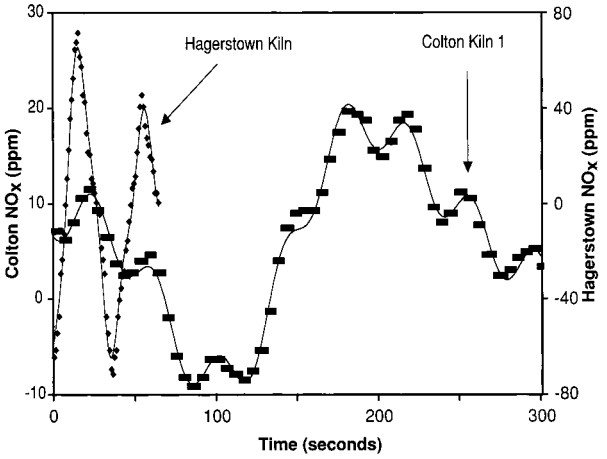

FIGURE 2. Short-term variation of NO_x emissions shown by residuals from the average of discrete readings of NO_x at 1-s intervals for kiln 1 of the California Portland Cement Company, Colton, CA, and residuals from the average of discrete readings of NO_x at 1.5-s intervals from the St. Lawrence Corporation kiln at Hagerstown, MD (*9*).

modified by intermediate-term oscillations which are overlaid by a very short-term (high frequency) oscillation. It is obvious from Figure 1a−c that the variations in the observed NO_x emissions from portland cement plants are frequent and large. These variations are probably due to changes of independent variables such as fuel, feed, air flow, and temperatures in the burning zone of the kiln in which fuel combustion and the sintering phase of the manufacture of cement clinker occur. Longer term variations in process control may be caused by changes in the type of cement that is produced and variations in the composition of the fuel and raw materials.

The 6-min and 1-h average data for the Crestmore, Maryneal, and Thomaston plants do not permit determination of the frequency characteristics of the short-term or random variations of NO_x concentration in emissions from cement kilns. Therefore, closely spaced instantaneous observations (not averages) of NO_x emissions were obtained from kilns at two additional cement plants to demonstrate the time characteristics of the very short-term variations and the random component. Figure 2 shows the short-term variation of NO_x concentrations in the exit gases from kiln 1 of the Colton plant owned by California Portland Cement Company and located at Colton, CA and the kiln of St. Lawrence Corporation's plant located at Hagerstown, MD. The lines in Figure 2 were obtained by least squares calculations for a six-term series consisting of three cosine terms and three sine terms. The periods for these terms for the Hagerstown data were 57.6, 48.6, and 20.8 s. Longer term variations were observed for the Colton data which had periods of 201.2, 114.3, and 39.2 s. The deviations from these least squares functions appear to be random in that both positive and negative deviations were observed.

Visual examination of the data in Figure 1a−c suggests that long-term nonperiodic variations around a mean value are present in the NO_x emission data from the Crestmore, Maryneal, and Thomaston kilns. These variations can be revealed by application of "low-pass" moving average filters to the data in Figure 1a−c. The averaging process removes the rapidly varying high-frequency component and emphasizes the nonperiodic oscillation of the emission values about mean values. However, this does not result in a straight-line value that approximates the mean. Oscillations are still present after application of a 90-day moving average filter on data from the Thomaston kiln.

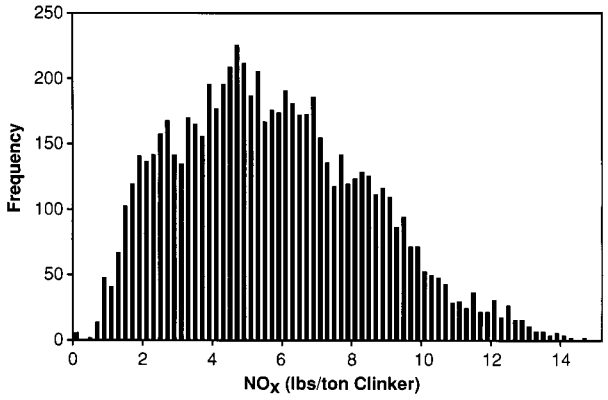

FIGURE 3. Histogram of 13 561 NO_x emission measurements for the Crestmore plant.

The NO_x emission rates shown in Figure 1a−c represent time series and must be statistically evaluated to determine if the individual values are independent and normally distributed. The frequency distribution (Figure 3) of NO_x emission values from the Crestmore plant approaches a normal probability distribution. This is also true for data from other cement plants. However, the individual values were not independent. Nonindependence of sequential NO_x emission measurements was confirmed by examination of autocorrelation functions and time series analyses of the emission data in Figure 1a−c. The lack of independence affects the calculation of the variance of the sample average of the emission rates from cement kilns. Therefore, many regulatory decisions which are based on assumptions of independence and the normal probability distribution may not be appropriate.

Autocorrelation and Time Series Analysis

The effect of time dependence in stationary time series data is often measured using the autocorrelation function. The autocorrelation function at lag k, denoted by ρ_k, measures the correlation between data values k time units apart. When no data are missing in a time series realization of length n, then ρ_k is estimated by

$$\hat{\rho}_k = \frac{\sum_{t=1}^{n-k}(Z_t - \bar{Z})(Z_{t+k} - \bar{Z})}{\sum_{t=1}^{n}(Z_t - \bar{Z})^2} \qquad (1)$$

where Z_t is the observed NO_x measurement at time t, Z_{t+k} is the observed NO_x measurement at time $t + k$, and $\bar{Z}$ is the mean of all n data values. However in the NO_x series, some data were missing because of periods when either the CEM was not functioning or the kiln had to be shut down for some maintenance operation. In the presence of missing data, modifications to the usual procedure must be utilized. We used PROC ARIMA from SAS (*10*) to calculate the autocorrelation estimates in this setting. When some data are missing, SAS only uses cross products in which both Z_t and Z_{t+k} are present. The ratio in eq 1 is adjusted using divisors that reflect the number of cross products available. Because of the desirability for the sample autocorrelations to be positive definite (*11*), a taper is applied if necessary in order to produce estimates with this property. These autocorrelation estimates will be denoted by $\hat{\rho}_k$. In Figure 4 we show the sample autocorrelations calculated using SAS based on the 13 681 data values for the Crestmore kiln, 5436 data values for the Maryneal kiln, and 11 767 data values for the Thomaston kiln.

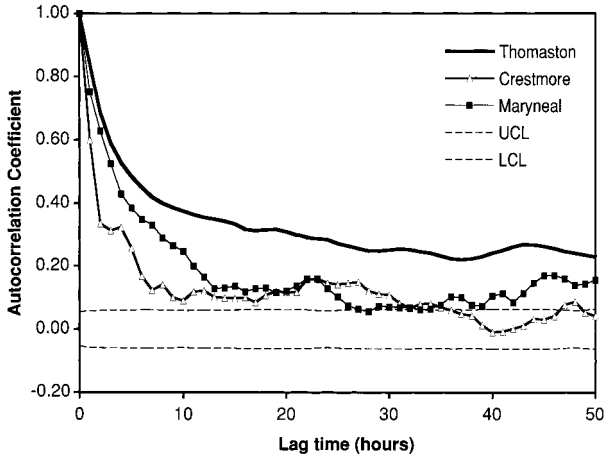

FIGURE 4. Autocorrelation functions for NO_x emission data from the Crestmore kiln (Figure 1a), Maryneal kiln (Figure 1b), and Thomaston kiln (Figure 1c). The 95% upper (UCL) and lower (LCL) confidence limits for the Maryneal data are shown for reference.

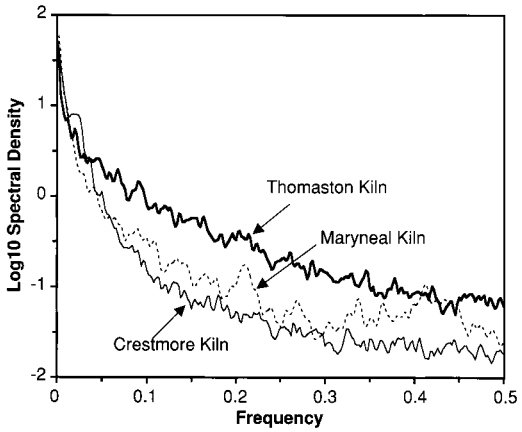

FIGURE 5. Spectral density estimates for the NO_x emissions from the Crestmore, Maryneal, and Thomaston kilns based on the respective autocorrelation function (Figure 4) for each kiln and eq 2.

The estimated autocorrelations are all large (and near one) for small lags. In contrast, if the data were an uncorrelated random series, then sample autocorrelations at nonzero lag would tend to be close to zero. The upper and lower confidence limits (at the 95% probability level) for the Maryneal autocorrelation function are shown in Figure 4 for reference. Maryneal sample autocorrelations that fall outside of these limits are significantly greater than zero.

The sample autocorrelations (Figure 4) for the Crestmore, Maryneal, and Thomaston data indicate that there is a strong association between sequential values of NO_x emissions. This association is evidenced by a strong peak at zero frequency in the spectral density estimates (Figure 5). We estimated the spectral density P using the Bartlett window (*12*) with truncation point, M,

$$M = 2\sqrt{n}$$

and frequency f. That is,

$$P(f) = 1 + 2\sum_{k=1}^{M}\lambda_k\hat{\rho}_k \cos 2\pi fk \qquad (2)$$

where

$$\lambda_k = 1 - \frac{k}{M}, \quad k = 0, 1, ..., M$$

$$\lambda_k = 0, \quad k > M$$

The association between data values was modeled for the Crestmore data (Figure 1a) and the Thomaston data (Figure 1c) as an autoregressive (AR) process using program GW (*12*). The GW program was limited to 500 data values in the time series and allows no missing data. Therefore, 17 subsegments of the Crestmore data consisting of 400−500 contiguous data values and 16 subsegments of the Thomaston data consisting of 300−500 contiguous data values were selected. The selected subsegments span the time-range of available data from both kilns. Another indication that the data are clearly autocorrelated is the fact that the Ljung-Box Portmaneau test (*13, 14*) rejected white noise at the 5% level of significance for each of the time series segments analyzed.

Model selection was based on examination of the Akaike's Information Criterion (*15*). All of the subsegments examined could be adequately modeled using an AR(p) model, eq 3, which has the form

$$Z_t = \alpha_1 \times Z_{t-1} + ... + \alpha_p \times Z_{t-p} + Y_t \qquad (3)$$

where the α_is are real constants and Y_t is uncorrelated, zero mean white noise. Thus, the NO_x emission rate at time t, Z_t, is given as a linear combination of the previous p emission rates plus a random component Y_t (*12, 14*). Parameter estimates were based on the maximum likelihood procedure. The models fit to the subsegments using AIC ranged from AR(1) to AR(19), with all models indicating strong autocorrelation at small to moderate lags.

Calculation of the Mean and Variance

The population variance of $\bar{Z}$ based on n uncorrelated observations is well-known to be

$$Var(\bar{Z}) = \frac{\sigma^2}{n} \qquad (4)$$

where σ^2 is the population variance. This variance is typically estimated by S^2/n where S^2 is the usual sample variance. However, when the data are correlated and there are no missing data, Box et al. (*14*) have shown that the variance of $\bar{Z}$ becomes

$$Var[\bar{Z}] = \frac{\sigma^2}{n}\left[1 + 2\sum_{k=1}^{n-1}\left(1 - \frac{k}{n}\right)\rho_k\right] \qquad (5)$$

The variance of $\bar{Z}$ could be estimated by inserting sample autocorrelations for the autocorrelations in eq 5. However, due to the high variability of ρ_k when k is near n, alternative estimates are often employed. Priestley (*11*) points out that for large samples, $Var(\bar{Z})$ in eq 5 can be estimated by

$$Var[\bar{Z}] = P(0)\frac{S^2}{n} \qquad (6)$$

where $P(0)$ is the estimated spectral density at frequency zero.

The spectral density at zero for the Crestmore, Maryneal, and Thomaston data was estimated as 57.87, 69.39, and 54.13, respectively. Thus, the proper estimates of the variance of the sample mean in these cases are 50−70 times higher than the usual estimate. Or said another way, the presence of autocorrelation in the data reduces the effective sample size by a factor of $P(0)$, that is by a factor of 50−70. Correspondingly, the standard errors adjusted for correlation (Table 1) are seven to eight times higher than those obtained using the usual formula (eq 4). Calculation of standard errors based on eq 4 results in a value that is too low.

TABLE 1. Descriptive Statistics of Time Series Data from the Crestmore, Maryneal, and Thomaston Kilns

moving av	mean	std dev	std error of the mean, eq 6	std error of the mean, eq 4
Crestmore NO_x data, lbs ton^{-1}	5.9	2.9	0.19	0.02
Maryneal NO_x data, lbs h^{-1}	234	42	4.7	0.57
Thomaston NO_x data, lbs h^{-1}	384	142	9.7	1.3

To empirically demonstrate the effect of autocorrelation on the variance of the sample mean, we consider NO_x emissions from the Hawaiian Cement Company plant located at Kapolei, HI. NO_x emission data, consisting of 12 978 1-min averages, were segmentally examined to determine the effect of calculating 30-min average values. The mean and standard deviation of all 12 978 values were 254.3 and 80.1 ppm, respectively. The individual NO_x emissions measurements in this data file ranged from a minimum of 11.7 ppm to a maximum of 666.4 ppm. To determine the effect of calculating averages of NO_x emission data, the parametric characteristics of 449 randomly sampled, 30-min segments of the time series were calculated. The largest mean of the 30-min segments was 575.7 ppm and the least was 80.4 ppm. The standard deviation of the 449 means of 30-min duration was 82.4 ppm. If the 1-min average NO_x values were independent, then the standard deviation of 30-min averages should be equal to $80.1/\sqrt{30} = 14.6$. The effect of autocorrelation, which was not calculated for this data set, was an increase in the expected standard deviation from 14.6 to 82.4, i.e., by a factor of 5.6.

Recommendations for Evaluation of NO_x Measurements

Misuse of statistical concepts based on independent and identically distributed data or independent and normally distributed data with data that is autocorrelated and not random can lead to erroneous conclusions unless the correct estimate of the population variance is used. Autocorrelation in process data effects the performance of control charts (*16, 17*). These effects result in both misidentification of outliers in the data and failure to detect other out-of-control values. Use of AR(p) models to identify the nonrandom effects result in improved process control (*16*). Appropriate control of NO_x emissions and establishment of emission limits requires correct data analysis and evaluation of emissions data.

Complexities inherent in the generation of NO_x from portland cement kilns result in inappropriate analyses of CEM data. The typically large number of data values and high apparent noise level may lead to the false visual impression that these data are independent. Regulatory limits and evaluations may be misapplied because the assumption is made that measurements of NO_x are independent and normally distributed. However, the degree of autocorrelation which is observed for NO_x measurements from portland cement kilns requires an alternative method of interpretation.

The population mean emission rate μ and population standard deviation σ for the NO_x emissions from a kiln can be estimated by the sample average of measured values and the calculated sample standard deviation S. Values of the mean and standard deviation represented by AR processes approach the population mean μ and standard deviation σ as the number of measurements become large (*18, 19*).

The amount of data required to make regulatory decisions should be that which results in an estimated variance of the mean NO_x emission rate, $Var[\bar{Z}]$ as calculated by eq 6 that is acceptably small. The variability of NO_x emission rates

suggests that both the absolute number of measurements and the degree of autocorrelation between sequential measurements are controlling factors. The time series analysis shows that the measured NO_x values cannot be averaged over a short period of time. This is especially true when a "few" grab samples are taken during a "source test". It is reasonable to approximate these statistics from continuous emissions measurements over a period of two to four weeks, provided no major independent variables are changed. However, the long-term variation inherent in the operation of a portland cement kiln results in drift of the calculated descriptive statistics until measurements encompassing all sources of variation are included in the data.

Determination of confidence limits of the mean or statistical tests related to the mean NO_x emission rate from a portland cement kiln must be made using the estimated variance of the mean as given in eq 6.

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