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A robust framework to predict mercury speciation in combustion flue gases

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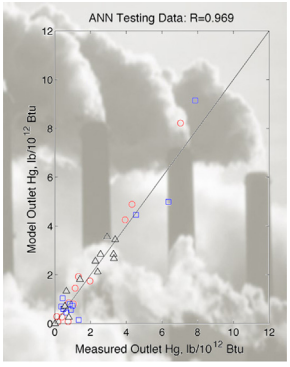
HIGHLIGHTS

- A model for mercury emissions from coal-fired power plants is presented and validated.
- The model only requires combustion temperature, coal heating value, and coal's Hg, S, Cl and ash contents.
- Post-boiler concentrations of elemental, particulate and oxidized mercury are well predicted ($R = 0.97$).
- Coal heating value, chlorine content, and combustion temperature are the most sensitive model parameters.
- For coal with Cl content >1000 ppm, elemental Hg emissions increase with temperature and Cl content.

GRAPHICAL ABSTRACT



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ABSTRACT

Mercury emissions from coal combustion have become a global concern as growing energy demands have increased the consumption of coal. The effective implementation of treatment technologies requires knowledge of mercury speciation in the flue gas, namely concentrations of elemental, oxidized and particulate mercury at the exit of the boiler. A model that can accurately predict mercury species in flue gas would be very useful in that context. Here, a Bayesian regularized artificial neural network (BRANN) that uses five coal properties and combustion temperature was developed to predict mercury speciation in flue gases before treatment technology implementation. The results of the model show that up to 97 percent of the variation in mercury species concentration is captured through the use of BRANNs. The BRANN model was used to conduct a parametric sensitivity which revealed that the coal chlorine content and coal calorific value were the most sensitive parameters, followed by the combustion temperature. The coal sulfur content was the least important parameter. The results demonstrate the applicability of BRANNs for predicting mercury concentration and speciation in combustion flue gas and provide a more efficient and effective technique when compared to other advanced non-mechanistic modeling strategies.

1. Introduction

Mercury emissions from combustion processes present a significant hazard to human health due to mercury's persistence and bioaccumulation potential in the environment. This potential health hazard has led to numerous regulations in the United States. For example, the Clean Air Mercury Rule was instituted by the United States Environmental Protection Agency (US EPA) in 2005 as part of an effort to reduce mercury emissions from coal-fired power plants [1]. Even so, global mercury emissions from coal-fired power plants are projected to increase significantly, as the demand for energy continues to increase in the next few decades

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[2]. The selection, sizing and efficacy of mercury control technology in flue gases depend heavily on the speciation of mercury, i.e., the respective concentrations of elemental, oxidized and particulate mercury in the flue gas [3–6]. Thus, accurate prediction of mercury speciation at the end of the boiler, i.e., prior to pollution control is highly relevant to design engineers that are tasked to select and size suitable mercury control.

To accurately assess mercury speciation in combustion flue gases, a number of mathematical models have been developed. In general, these models seek to estimate mercury speciation by considering coal characteristics and combustion conditions. One common approach to modeling these systems is the use of kinetic reaction and equilibrium speciation models [7–11]. These conceptual models require a large number of measurements and a very detailed understanding of combustion and mercury reaction mechanisms. These processes are often nonlinear and thus difficult to assess using conventional rate based differential equations without a complete mechanistic understanding.

However, in the last two decades, a number of artificial intelligence (AI) techniques have been developed that could be utilized to address this problem. Artificial neural networks (ANNs) are one such technique that has been successfully used in a number of chemical and environmental applications [12–20], including pollutant emissions prediction. The use of ANNs has increased because of their superior ability to solve complex, non-linear problems without any requirement for mechanistic understanding of the process being modeled. ANNs have been successfully applied for mercury speciation, though their ability to be used for data prediction has thus far been limited. Jensen et al. [21] utilized a general backpropagation ANN to model mercury speciation in combustion flue gases using mercury concentration, heating value of coal, chlorine content, sulfur content, ash content, and temperature as explanatory variables. The results of this study showed the ability of ANNs to predict mercury species concentration, although the validation set only contained a small subset (one input dataset) of the 82 total plants in the available data set obtained by Jensen et al. [21]. Another study from Abdel-Aal [22] reports utilizing a group method of data handling (GMDH)-based neural network to model the same data set utilized by Jensen et al. [21]. This approach achieved correlation coefficients as high as 0.97 for training data, although the results of the validation sets contained increased scatter. This is a common problem encountered when a method has overfit the training data.

Recently, another empirical technique known as support vector machines (SVM) was used by Zhao et al. [23] to predict speciation of mercury in flue gases. The SVM approach was able to achieve a correlation coefficient, $R = 0.92$, for the validation set, a vast improvement over the other studies by Jensen [21] and Abdel-Aal [22]. A number of ANN techniques were also tested in the same study by Zhao et al. [23] in which the results indicated that the SVM was the most accurate approach for modeling mercury speciation in flue gas [23].

A more advanced technique for network weight optimization, known as Bayesian regularization, has been developed and it has been shown to be superior compared to general backpropagation algorithms [24,25]. The advantage of the Bayesian regularization is that it considers the network weights probabilistically, which allows pruning unnecessary architecture (i.e., hidden node connections), thereby reducing the risk of overfitting the training data set. Thus, in this work, a Bayesian regularized ANN was utilized in an attempt to obtain a more accurate and predictive model of mercury speciation in combustion flue gases prior to pollution control equipment. The prediction performance of this model was compared to that of the other AI techniques applied for mercury speciation studies to determine the effectiveness of the Bayesian approach. Finally, an interpretation of network weights was performed to determine the relative importance of input parameters on the generalization ability of the ANN. These parameters were used to create a response surface plot from which parametric sensitivity could be visualized.

2. Methods

2.1. Sample data and input parameters

The dataset used for this study was collected as part of the Information Collection Request (ICR) [26] by the US EPA. It contains elemental, particulate, and oxidized mercury concentrations from 82 coal-fired power plants in the United States. It is the same dataset used by major studies of mercury speciation in flue gases [21–23], and will thus provide a good measure of model applicability.

For modeling purposes, six parameters key to mercury emissions from coal combustion were considered, consistent with earlier studies (Table 1). One of the parameters (outlet flue gas temperature) is determined by the operating condition of the plant, while the other five parameters are specific to the coal undergoing combustion.

2.2. Model formation procedure

In order to obtain representative training and testing sets, a K means clustering algorithm on the input and output data vectors was used to partition the data into subgroups. This clustering technique and is widely recognized to provide a full and representative description of the entire parametric space, thus resulting in the most accurate model structures for the given data set [24]. The ten cluster subgroups were then divided randomly into training (85% of data) and testing (15% of data) so as not to bias the model results. The use of a clustering algorithm ensured that both the training and testing datasets were representative of the same population, reducing the potential error associated with random data partitioning techniques often used in ANN models. It is important to note that the training and testing sets were chosen by plant, not by individual species datum. Thus, during clustering, all three measurements (i.e., elemental, oxidized, and particulate mercury) from a given plant were either included in the training or the testing data sets.

Due to the large differences in input parameter values (e.g., chlorine content varying by five orders of magnitude), a linear normalization procedure served to scale the data to a 0.1–0.9 interval. This procedure was performed on both the input and output data, whereby a reverse transformation was performed at the end of the simulation to obtain the model outputs with the correct unit.

2.3. Bayesian regularization

Bayesian regularization is a mathematical technique that seeks to solve ill-posed problems by introducing information in the form of a penalty for complexity [27]. Bayesian methods are useful for neural networks because of their inherent ability to penalize overly complex models, reducing the risk of fitting data noise, often termed overfitting. Since these networks penalize complexity, they are generally insensitive to the size of the network as long as the minimal architecture has been specified [24].

In standard backpropagation algorithms a single set of parameters is used to optimize the network for function fitting and pattern recognition. However, the Bayesian method utilizes all possible values of the parameters and weights to determine the optimal architecture. Neural network layer weights are generally updated and optimized by reducing some cost function, often mean squared error, shown below:

$$F = E_D = \sum_1^n (\text{measured}_i - \text{modeled}_i)^2 \quad (1)$$