Uncertainty Analysis on Process Organized Emission Inventory in Petrochemical Enterprises of Hainan Province

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Abstract. The study qualitatively and quantitatively evaluated the uncertainty of the emission inventory of SO₂, NOx, particulate matter (PM) and non-methane volatile organic compounds (NMVOCs) based on the measurement method in the process of organized sources in eight typical petroleum refining enterprises in Hainan Province in 2017. According to the TRACE-P inventory grading, the activity level data uncertainty was between I and II, and the emission factor rating was roughly C-level. The qualitative assessment of the emission inventory is “good”. The Monte Carlo simulation model was used to quantitatively evaluate the uncertainty. The results show that the uncertainties in emission inventory of SO₂, NOx, PM and NMVOCs are ±2.9%, ±6.3%, ±7.6% and ±13.7%, respectively, with the highest uncertainty in NMVOCs emissions. The study on emission inventory uncertainty will help decision makers to scientifically formulate air pollutant control strategies for the accessibility of pollutant emission reduction targets of petrochemical enterprises and guide the improvement of emission inventory and data collection.

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1. Introduction

In the decision support technology system of air quality management, the establishment of accurate, complete and timely emission inventory of atmospheric pollutants is the basis and prerequisite for identifying pollution sources and carrying out air pollution prevention and control scientifically and effectively. It is also the important foundation and basis for formulating the environmental air quality standard planning and the emergency plan for heavily polluted weather [1-2]. However, there are uncertain factors such as unavoidable monitoring error, random error, lack of key data, and insufficient representation of data in the estimation and analysis of the emission inventory, which brings uncertainty [3-4]. Through the qualitative and quantitative analysis of various uncertain sources of the inventory, the uncertainties and possible ranges of the emission inventory are determined, and the main factors leading to the uncertainty of the inventory are identified, which will play an important role in improving the inventory. Given the importance of uncertainty in improving inventory quality...
and reducing inventory uncertainty, including the requirements of important agencies and government organizations of the Intergovernmental Panel on Climate Change (IPCC) [5-6], the United States Environmental Protection Agency (US EPA) [7], and the European Environment Agency (EEA) [8], uncertainty analysis and results should be an important part of the emission inventory establishment and research reports.

The uncertainty of emission inventory refers to the lack of knowledge and understanding of the true value of the inventory, which can be assessed by qualitative and quantitative methods [4]. The data quality rating method is commonly used in qualitative analysis [9-10], although large amounts of resources are not required in qualitative analysis, the emission inventory uncertainty cannot be quantitatively recognized. Quantitative assessment methods of inventory mainly include quantitative uncertainty analysis of relevant model inputs such as emission factors and activity data level, and quantitative transmission of uncertainty in the emission inventory estimation model. Quantitative uncertainty analysis of model input can use “central limit theorem” and statistical methods based on “bootstrap simulation” as well as expert judgment. The transmission of uncertainty in the emission inventory model is mainly based on the error transmission method or the Monte Carlo simulation method, which has been widely used as a result of its flexibility [11-13]. In the Monte Carlo simulation method, one value is randomly extracted from the model input, and the corresponding model output size is calculated; after n times of repeated sampling, the probability distribution constituted by n model outputs represents the model outputs, thus the uncertainty of emission inventory is quantified. The Monte Carlo method is like a simulation tool, which transforms the problems analyzed into probabilistic problems and solves them by stochastic methods; it can be used to analyze the accumulation of different categories or the uncertainty of the whole inventory category level in order to improve the inventory accuracy. This method is also the main one for quantitative analysis of the established emission inventory in this study.

In this study, the flow velocity, flow rate and pollutant concentration of the main pollutants (SO$_2$, NOx, PM and NMVOCs) in the organized emission process of typical petrochemical enterprises in Hainan Province were determined by the measurement method. The corresponding pollutant emission information was obtained through calculation and transformation, and the process organized emission inventory of typical petrochemical enterprises in Hainan Province was established. The uncertainty of the inventory was assessed by qualitative and quantitative methods to provide scientific reference and basis for the treatment of process organized pollution emission in the petrochemical industry Hainan Province.

2. Materials and Methods

2.1 Detection of process organized emission pollutants from petrochemical enterprises

The pollutants measured in the organized emission process of petrochemical enterprises mainly included SO$_2$, NOx, PM and NMVOCs. The analysis methods of pollutants shall be carried out according to the relevant technical standards issued by the Ministry of Ecology and Environment. The laboratory analytical methods and instruments for each pollutant are shown in Table 1.

| Pollutant | Reference standard | Instrument | Detection limit (mg/m$^3$) |
|-----------|--------------------|------------|-----------------------------|
| SO$_2$    | HJ 57-2017         | Portable flue gas analyzer | 3 |
| NOx       | HJ 693-2014        | Portable flue gas analyzer | 3 |
| PM        | HJ 836-2017        | Portable Low Concentration PM Tester | 1 |
| NMVOCs    | HJ/T 38-2017       | Gas chromatograph       | 0.1mg/L |

2.2 Calculation of process organized emission inventory

Process organized pollution sources referred to the process or equipment that discharge pollutants (VOCs) through exhaust funnel of over 15m or vent nozzle in addition to combustion flue gas
pollution sources and torches in the production process of petrochemical enterprises, which belonged
to the fixed point sources. Practical measurement of process organized emissions could reduce
assumptions about the data applicability of emission sources, fuel characteristics and effectiveness of
control measures. The formula of offline detection to estimate pollutant emissions is as follows [14]:

\[ E_i = \sum_{n=1}^{N} \left\{ Q_n \times \left[1 - \left( f_{H_2O} \right)_n \right] \times \frac{T_n}{T_o} \times \frac{P_o}{P_n} \times \left( C_i \right)_n \times H \times 10^{-9} \right\} \]  

Where: \( E_i \) is the emission of pollutant \( i \), t/a. \( N \) is the number of measurements throughout the year;
\( n \) is the measurement No., the \( nth \) measurement; \( Q_n \) is the flow rate (wet basis) of the process exhaust
gas at the \( nth \) measurement, m\(^3\)/h; \( \left( f_{H_2O} \right)_n \) is the water content and volume fraction of process
exhaust gas at the \( nth \) measurement; \( T_o \) is the temperature of standard state, 273.15 K; \( T_n \) is the
temperature at the \( nth \) flow measurement, K; \( P_n \) is the average pressure at the \( nth \) flow measurement,
kPa; \( P_o \) is the average pressure of standard state, 101.325 kPa; \( (C_i)_n \) is the concentration of pollutant \( i \)
(dry base and standard state) in the process exhaust gas at the \( nth \) measurement, mg/m\(^3\); \( H \) is the time
interval between two measurements.

2.3 Uncertainty assessment method

2.3.1 Qualitative assessment method

Uncertainty assessment of inventory was to identify the possible factors affecting the estimation
results in the process of compiling emission inventory, which was reflected in the uncertainty analysis
of each emission factor and activity level data. The basic working ideas were as follows: Firstly, how
to obtain activity level data in the process of data collection, and how about its reliability and accuracy?
Secondly, what were the sources and representativeness of emission factors? Finally, how was the
applicability and representativeness of the emission inventory estimation model?

Activity level information was obtained either directly from industry and enterprise statistical
bulletin data or by using related technical indicators to distribute statistical bulletin data, or by using
conversion coefficient calculation based on other relevant statistical bulletin data. The activity level
information data quality assessment system refers to the empirical values of TRACE-P list [15], as
shown in Table 2.

| Level | Acquisition mode | Judging basis | Uncertainty |
|-------|------------------|---------------|-------------|
| I     | Directly from statistical data | ----- | ±30% |
|       | Statistical data distributed by distribution coefficient: | High reliability of distribution coefficient | |
| II    | Based on other statistical information, estimated by conversion coefficient | 1. High correlation of statistical information; 2. High reliability of conversion coefficient; 3. The estimated results have been verified. | ±80% |
| III   | Based on other statistical information, estimated by conversion coefficient | 1. High correlation of statistical information; 2. High reliability of conversion coefficient; 3. The estimated results have not been verified. | ±100% |
| IV    | Based on other statistical information, estimated by conversion coefficient | 1. High correlation of statistical information; 2. Low reliability of conversion coefficient. | ±150% |
Based on other statistical information, estimated by conversion coefficient:

1. Low correlation of statistical information;
2. Low reliability of conversion coefficient ±300%

The emission factors in this study were mainly based on the Guidelines for the Investigation of VOCs Pollution Sources in Petrochemical Industry issued by the Ministry of Ecology and Environment and Pollutant Emission Factor Document (AP-42) issued by the US Environmental Protection Agency. The AP-42 emission factor database was classified according to the number of tests. Among them, the emission factors of more than 10 similar pollution sources tested by the same measurement technique were A-level; the emission factors tested from a few pollution sources were B-level; the emission factors derived from investigation collection or emission factors of similar pollutant emission process were C-E-level.

Finally, based on the qualitative assessment results of activity level data and emission factors, after comprehensive analysis, four levels of “excellent”, “good”, “medium” and “poor” were set up to qualitatively analyze the uncertainty of the inventory.

2.3.2 Quantitative assessment method

In this study, the Monte Carlo simulation method was used to analyze the uncertainty transmission of inventory. The basic principle of Monte Carlo method was to select random values on the individual probability density function of input values and calculate corresponding output values; after being repeated multiple times, each calculation result constituted the probability density function of the output value; when the average of the output value didn’t change, the repeated calculation could be ended. The overall average value and uncertainty was obtained based on the repeated calculation results and the probability distribution law of emissions.

Fig.1 shows the main steps of the Monte Carlo method in calculating the inventory uncertainty. Firstly, the probability distribution of each parameter, such as normal distribution and uniform distribution was determined. Then, the values of each parameter were extracted independently, and the extracted values conformed to their probability distribution. The emissions of each pollutant were simulated according to the inventory calculation method, and the random sampling value in the previous step was used to substitute the corresponding inventory calculation method to calculate the emission load under the sampling group. Finally, the simulation was repeated to obtain larger samples to simulate the probability distribution law of pollutant emissions, in order to obtain the overall average value and uncertainty.

In this study, 95% confidence interval was used to quantify the random error; the corresponding emissions with cumulative probability density of 2.5% were taken as the lower limit and 97.5% as the upper limit.
3. Results and Discussions

3.1 Emission inventories of petrochemical enterprises in Hainan Province in 2017

Through the measurement and investigation of the air pollutants concentration, discharge flow, working time of the process organized emissions in two typical petrochemical enterprises in Hainan Province, the major pollutant emissions such as SO$_2$ and NO$_X$ from the two enterprises were calculated. Enterprises without field measurement adopted linear regression algorithm to estimate according to their product output characteristics and measured values, and finally obtained the emissions of process organized pollutants of eight typical petrochemical enterprises in Hainan Province, as shown in Table 3.

It can be seen from Table 3 that the emissions of process organized discharge from petrochemical enterprises in Hainan Province is the largest, reaching 3866.0 tons. The essential raw material in petrochemical enterprises - petroleum contained a certain amount of sulfur, and a large amount of SO$_2$ was generated when petroleum was used to produce fuel products and chemical products[18]. Therefore, it is very important to conduct well sulfur recovery and desulfurization in petrochemical enterprises. NMVOC was the second largest pollutant in terms of emissions, reaching 2958.9 tons. The petrochemical enterprises had various chemical products and complicated emission links, which were the important emission sources of NMVOCs. Among the numerous emission links, NNVOCs leakage and dissipation were important ones[19-20]. The tropical monsoon climate with high annual temperature in Hainan Province aggravates the volatilization of NMVOCs and increases the emission of NMVOCs. The emission of NOx from petrochemical enterprises in Hainan Province reached 1779.8 tons; nitrogen oxides in petrochemical enterprises mainly came from process heating furnaces and FCC regeneration flue gas; nitrogen oxides and volatile organic compounds were important precursors of ozone generation, when petrochemical enterprises discharged large amounts of these two pollutants simultaneously, ozone generation could be promoted, causing secondary pollution. Thus it is urgent to effectively control these two pollutants in petrochemical enterprises.

![Diagram of Monte Carlo numerical analysis of inventory uncertainty working steps](image-url)
### Table 3 Emission inventory results of organized discharge from petrochemical enterprises in Hainan Province

| Pollutant | Emissions (t/a) |
|-----------|----------------|
| SO$_2$    | 3866.0         |
| NO$_x$    | 1779.8         |
| PM        | 338.5          |
| NMVOCs    | 2958.9         |

#### 3.2 Uncertainty assessment results

#### 3.2.1 Qualitative evaluation results

Most of the research activity level information was directly derived from industry and enterprise statistical bulletin data, and a fraction of was obtained by using relevant technical indicators to distribute statistical bulletin data. According to the TRACE-P inventory grading\cite{15}, the uncertainty was between I and II.

The emission factors of this project mostly adopted Guidelines for the Investigation of VOCs Pollution Sources in Petrochemical Industry issued by the Ministry of Environmental Protection\cite{16} and Pollutant Emission Factor Document (AP-42)\cite{17} issued by the US Environmental Protection Agency. In view of the differences between the test samples and natural conditions in the region, the emission factor rating was roughly C-level.

Based on the above assessment results, the qualitative assessment of the emission inventory of this project was “good”.

#### 3.2.2 Quantitative assessment results

In this study, Monte Carlo method was used to quantitatively analyze the uncertainty of NO$_x$, SO$_2$, PM and NMVOCs in the inventory process. Assuming that the input data was in the form of normal distribution, the probability density distribution of pollutant emissions was obtained by 5000 sampling times (of which NMVOCs were sampled 20,000 times). Taking 95% confidence interval, the simulation results of four pollutants uncertainty are shown in Fig. 2.

Fig. 2 indicates that the average value of simulated SO$_2$ emission is 3978.3 t, 95% the probability distribution range is 3958t~3999t, and the uncertainty is (-2.9%~+2.9%). The average value of simulated NOx emission is 1892.4 t, 95% the probability distribution range is (1873.0 t to 1912.0 t), and the uncertainty is (-6.3%~+6.3%). The average value of simulated PM emission is 364.3t, the 95% probability distribution range is (305.2t~422.8t), and the uncertainty is (7.6%~7.6%). The average value of the simulated NMVOCs emission is 3853.0 t, 95% the probability distribution range is (3533.1 t~4171.5 t), and the uncertainty is (-13.7%~+13.7%). Comparisons showed that the uncertainty of SO$_2$, NOx and PM emission inventory was relatively small, and the average values of simulated emission were not much different from the actual estimated values. Therefore, the emission control of these three pollutants could be carried out according to the estimated results of this study. The uncertainty of NMVOCs emission results was relatively large, and the difference between the mean value of model simulation and the actual estimation results was large. The reason for this uncertainty was that there were numerous organized emission links in eight petrochemical enterprises, and the characteristic pollutants in different emission links were quite different, which led to the difference of emission characteristics of NMVOCs in primary discharge. On the other hand, due to the high volatility and reactivity of NMVOCs\cite{21,22}, there were losses in the process from field sampling to laboratory testing, resulting in the large uncertainty of NMVOCs inventory. The uncertainty should be fully considered in the treatment of NMVOCs.
Fig. 2 Uncertainty analysis of SO$_2$, NOx, PM and NMVOCs emission inventory

4. Conclusions
(1) In 2017, the emissions of SO$_2$, NOx, PM and NMVOCs in eight typical petrochemical enterprises in Hainan Province were 3886.0 tons, 1779.8 tons, 338.5 tons and 2985.3 tons, respectively. Petrochemical enterprises discharging a large amount of NOx and NMVOCs at the same time plays a great role in promoting the generation of ozone, hence it is significantly important to control the pollutant emission from petrochemical enterprises

(2) According to the TRACE-P inventory grading, the activity level data uncertainty of SO$_2$, NOx, PM and NMVOCs emission inventory was between I and II, and the emission factor rating was roughly C-level. The qualitative assessment of the emission inventory is “good”.

(3) The Monte Carlo simulation model was used to quantitatively evaluate the uncertainty. The results show that the uncertainties in emission inventory of SO$_2$, NOx, PM and NMVOCs were $\pm 2.9\%$, $\pm 6.3\%$, $\pm 7.6\%$ and $\pm 13.7\%$, respectively, with the highest uncertainty in NMVOCs emissions.

(4) The study on emission inventory uncertainty is necessary. It will help decision makers to scientifically formulate air pollutant control strategies for the accessibility of pollutant emission reduction targets of petrochemical enterprises and guide the improvement of emission inventory and data collection.

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