Regression modeling to predict ultrafine particles emission in a mineral plant combining meteorological and process variables

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Abstract

Ultrafine particles are object of main health concern, but its concentration is challenging to be continuous monitored in mineral and metallurgical industrial processes. This paper shows the development of an empirical regression model correlating the ultrafine particles concentration measured by two continuous analyzers, electrodynamic (EDA) and optical scatter (OSA) with meteorological and process parameters. The analyzers were installed at stack of an industrial mineral fertilizer plant over 4 seasons. The results showed that EDA have poor correlation with process or meteorological parameters (r-squared less than 10%) what can be caused by particles not being charged evenly on the stream as its better accuracy for particles over 10µm, as previous studies had suggested. The OSA ultrafine particles concentration model showed r-squared of 45% correlation with meteorological parameters and raw material feed. The model presented and standard error of 0.21 mg/Nm$^3$ which is considered adequate for industry compliance purposes. OSA shows promising application if meteorological parameters are included, as already in practice for ultrafine particles monitoring outdoors.

Keywords: Continuous dust analysers; Ultrafine particles; Regression model; Mineral fertilizer.

1 Introduction

The mineral fertilizer industry produced in 2018 around 62 million tons of ammonium nitrate/ calcium ammonium nitrate (AN/CAN) over the world [1]. When producing AN/CAN there is emission of ultrafine particles (UFP) mainly formed in gas phase, no matter which production process is employed but, when using prilling towers (PT) the issue becomes critical due to the high air flow needed. Besides that, their health impact is significant once the human exposure to particulate matter (PM) is correlated with an increase in cardiac and respiratory morbidity and mortality [2].

Combining the transient nature of UFPs with stricter regulations in place from WHO [3] regarding concentration level of called PM1 (dust with diameter below 1000nm) being reviewed and intended to be published in 2020 the need for accurate continuous monitoring of these type of particles with existing methods and equipment is urgent to be evaluated and validated.

1.1 Mapping of potential parameters in prilling fertilizers with AN/CAN

The approach here employed was to identify which meteorological and process parameters could potentially influence the UFP emission or the reading of those instruments, defining a system which includes inlet and outlet parameters of the prilling tower under study.

1.2 Ultrafine particle concentration methods

There are standard and reliable methods to measure concentration for PM10 and for PM2.5 (±10% error for PM2.5) yet not continuous, developed and validated [10] but per authors knowledge nothing similar is available for UFP. Studies concerning UFP shows a difference between...
methods (light scattering and personal gravimetric samplers) at a factor of 2.23, for instance in an in-mine application [11].

Galvão et al. [12] when studying trends in analytical techniques applied to particulate matter characterization highlighted the importance of the knowledge of particles properties, sampling even in a controlled environment as the laboratory.

The measurement of semi volatile UFP, for instance, is discussed by Wilson et al. [10] specially in the case of sulfates and nitrates where the concentration and composition changes due to the process but also to the location and season.

The commercially available PM analyzers are based mainly on two principles, electrodynamic and optical trap or scatter [13]. The electrodynamic balance (EDA) stably traps charged aerosol particles by balancing the aerosol particle in an electric field. This stable trap is sensitive to changes in mass. On the other hand, OSA trap uses a laser beam passing through the flow creating an optical trap. OSA can trap smaller particles up to hundreds on nanometers.

### 1.3 Modelling techniques for experimental data

Modelling experimental data is widely used, however few papers deal with particulate matter (6121 research papers from 2010 until 2020) and just 8 were found to be related to stationary sources, from those only one is regarding UFP or PM less than 1µm [14]. These figures show the gap between the stricter regulations by WHO and governmental agencies over the recent years and the level of maturity on this research field.

Statistical methods help understanding variables responses in experimental investigations among many engineering related areas. A web-search on Science Direct platform in 2019 by the authors showed that for the last 10 years response surface methodology, linear regression model and artificial neural network model were the most employed methods while in research related to particulate matter emission authors as Padoan et al. [15] for road dust emissions, Moser et al. [16] for aerosol emission on post combustion pilot plant have applied regression models.

Consistent with the technology scenario described, this paper aims to develop empirical models based on regression, for two distinct online analyzers installed at stack of a fertilizer industrial plant, correlating the UFP concentration to process and meteorological parameters over four seasons in Europe. Finally, there will be evaluated if the method current in use for UFP ambient monitoring can be applied to industrial stationary stacks.

### 2 Methodology

This work was performed at an industrial mineral fertilizer plant, where more than 40 different grades are currently produced. The potential set of candidate variables included both process and meteorological parameters. The particle characterization was performed with ELPI+ and the concentration at the stack monitored with both optical scatter and electrodynamic trap techniques. The results from four seasons monitoring was examined employing Minitab 19th.

#### 2.1 Industrial process set-up

The process is based on reaction from phosphate rock and nitric acid and after some separation steps the called mother liquor is mixed with potassium chloride and ammonia (also some formulas take small amounts of other nutrients source), generating a melt in high temperature (over 140°C) which is pumped to a centrifugal bucket with small holes inside the Prilling Tower (PT) [5]. As showed in Figure 1, the melt droplets fall in the tower and are cooled down by ambient air in counter-current flow. The UFP is carried to the top of the PT by 6 fans connected to their respective stack. The analyzers were installed at the same position where
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gravimetric sampling takes place, 20 diameters after top of PT and 3 diameters before the end of stack.

2.2 Characterizing and measuring concentration of UFP

In order to characterize the PM emissions from stack, ELPI®+ [17] was employed, once it can provide online concentration and PSD (particle size distribution) changes in the continuous process and still keep samples in 14 different stages to estimate its composition. The aluminum foils were pre-greased to avoid re-entrainment for the next stages.

A design of experiments was performed (second order with middle point) with a grand total of 9 tests each with duration of 30min under same product but different meteorological conditions to evaluate the PSD of the emissions at stack. The concentrations are expressed in mass.

To collect enough material to chemical characterization a test was performed under stable operation until the impactor ELPI+ was full (the pressure drop over the impactor can no longer be kept under 35mbar). The aluminum foils from each of the 14 stages was analyzed with SEM/EDS (scanning electron microscopy / energy dispersive x-ray spectroscopy).

Two continuous monitoring sensors from PCME [18] were installed at stack, being optical scattering analyzer (OSA) model PCME QAL 181 with certification range of 0-15mg/Nm$^3$ and measurement capability of 0-300mg/Nm$^3$ and electrodynamic analyzer (EDA) model PCME STACK 980 with certification range of 0-15mg/Nm$^3$ and measurement capability of 0-500mg/Nm$^3$.

2.3 Dataset preparation and regression techniques

To develop the model, data from three different sources was collected. The DCS (Distributed Control System) from the plant operation, meteorological data from the closest meteorological station and finally the output from two continuous dust analyzers (OSA and EDA).

Meteorological data such as temperature, wind speed, relativity humidity (RH) and precipitation were collected from the nearest measurement station (1.2km far from the stack monitored in straight line). The results were available in hour average basis.

There were employed 6,215 complete hourly data sets, representing 344 days under stable mass flow (product mass flow from 60 to 180 t/h).

For the statistical analysis of data set it was used Minitab® 19 software and linear regression models. The statistical indicators considered here will be coefficient S (standard error in the regression), r-square which is the percentage of response variation explained by a linear model. The significance of parameters will be evaluated by p-value, F-test and residuals.

3 Results and discussions

3.1 Characterization of PM under study

The result of characterization of PM is presented in Figure 2 where the confidence interval for the mean is 95%. The PM has a monodisperse distribution with a median of aerodynamic diameter of 1.23µm from 9 tests performed. The particles smaller than 1.24µm represent 78% of the mass distribution. When taking into account the number of particles, up to 93% of particles are smaller than 0.75µm leading to classify them as ultrafine particles [19,20].

Soysal et al. [19] when discussing the challenges of measuring concentration for fine PM highlight that ELPI measures current in real-time but demands the previous knowledge of effective density. In this case the effective density set on ELPI+ was 1.36 g/cm$^3$ for ammonium nitrate compounds [21].

Figure 1. Industrial Prilling Tower (PT) set-up.

Figure 2. PSD of mineral fertilizer aerosol in each impactor stage.
Samples of the PM collected over a long test (5 h sampling) were taken to SEM/EDS in order to understand their composition, although only stage 1.24µm gave significative results. The other stages contained very small amount of sample, even after 5 h sampling time, that was not possible to determine its concentration.

Figure 3a shows the foil under study. One of the agglomerates is showed on Figure 3b with 180 times magnification and a further increase to 1500 times magnification is presented on Figure 4 which one shows 3 different types of particles, marked as A, B and C. There is a region where the main area is covered by gray particle agglomerates (A). In the center of the image there are some potential single light-gray particles (B) and next to it some white agglomerate (C).

The results found from SEM/EDS excluded Aluminum from the detected elements due to the fact the foil (substrate) is made of Al. Besides that, no source of Aluminum is used in this plant. Later, the presence of Carbon was found to be due to the grease applied on the aluminum foil to ensure attachment of particles to the foil surface and avoid re-entrainment.

The chemical composition of the UFPs presented in Figure 4 suggests that the main component here is ammonium nitrate what is in accordance to the effective density parameter inputted in the ELPI+ (area A). Area B has composition that potentially can be FNO₃, SiF₄, in addition to the carbon from the greased foil, while area C shows the ammonium chloride aggregated. In this area the shape and color are in agreement with the crystal description.

With the knowledge of the product composition under handling in the prilling tower having 21% nitrogen, 11% potassium, 6% phosphorous and 4.4% sulfur, no correlation was found with UFPs composition what leads to conclude

Figure 3. (a) Stage 1.24µm support, Al foil, substrate and UFPs; (b) One UFP agglomerate.

Figure 4. (a) Magnification of 1500 times of UFP agglomerate with particles named as A, B and C and (b) Chemical composition of A, B and C.
that most part of the emissions come from the reactions in gas phase, once no phosphorous neither potassium was found on the chemical mapping of the emissions. Also, ammonium nitrate can evaporate, under equilibrium up to 50% of its mass, in size ranges from 1 to 2.5µm while ammonium sulphate up to 25% of its mass under same conditions [10], leading to potential large deviations when comparing concentration measured using ELPI+ with gravimetric sampling.

3.2 EDA UFP concentration as a function of process and meteorological parameters

When correlating the process and meteorological parameters with the output of EDA, the best correlation result found was when employing Box-Cox transformation with optimal lambda equal to -0.40. Based on this transformed response S was equal to 0.28 mg/m³ and r-squared of 9.49%. The F-test for the regression model obtained was 53.91 and p-value equal to 0 what so the model obtained is considered significant.

Parameters as liquor and salts flow to PT, mixer rotation, bucket rotation and wind speed are not significant by the criteria here applied (significance level of 5%). The resulting model can then be written as per Equation 1.

\[-EDA^{(-0.40)} = -1.220 + 0.000680 \text{NH}_3 \text{to PT} + 0.001303 \text{Off-spec flow to PT} + 0.000295 \text{Liquor temperature} - 0.00916 \text{Air temperature} + 0.010916 \text{Melt temperature} + 0.04463 \text{Precipitation} + 0.003288 \text{RH\%} \]

(1)

The air temperature is by far the most significant parameter in the model, followed by RH\% and precipitation.

Only two other process parameters have significance, being liquor temperature and NH\(_3\) flow, what is not consistent to behavior found by other authors as Séquier et al. [4], Couper et al. [6], Wu et al. [22], Wong et al. [8] and Shirley et al. [9]. Once there is data available for the ambient air just in meteorological station, not in the stack itself, it remains the question on if is RH\% influencing or not the output of EDA.

The analysis of residuals from Figure 5 shows the difference between predicted values by the model and measured results.

The residuals are basically dispersed in the range 0 to 20 mg/Nm\(^3\) (employing the calibration factor of 5.45 mg/Nm\(^3\) to u/m\(^3\) which is the raw reading of the sensor EDA) what indicates that some parameter is missing in the analysis [23].

Based on the literature studied when building the model, no potential relevant variable was left aside that could explain such a poor fit of the model besides what was already mentioned for Figure 5 regarding the meteorological parameters monitored from the closest station. Sullivan et al. [13] point out that the electric field strength required to stably trap the particle provides an accurate real-time measurement if the charge state is known although tests for single particles have being performed only on the range greater than 10 µm in diameter. None similar study was found for UFPs by the knowledge of authors.

3.3 OSA UFP concentration as a function of meteorological and process parameters

The best regression model for OSA PM concentration was obtained by Box-Cox transformation with lambda equal
0 (natural log) where the standard error found was 0.72 (equivalent to 0.21mg/Nm³), r-squared equal to 45.25% and F-value of 425 with p-value equal to 0.0 what can be considered significant model result once in this process under study the “Best Available Technique” emission is 5mg/Nm³ [24] and the standard error here found is equivalent to only 4.4% over the whole year monitored.

Also, the inclusion of the constant term in the model ensures that all non-explained effects are considered. When not including the constant term in the model the r-squared for the same data set would be 96.34%, although not realistic. Once no such model has been found in the literature a comparison was made with authors studying ambient air modelling. Padoan et al. [15] for example found a r-squared of 74% when modelling road dust emissions with a much smaller data set while Xu [25] found 60 to 80% r-squared using dust aerosol optical depth with PM10 results and Sieniutycz and Szwast [26] with neural networks were able to predict PM10 with 75 to 86% r-squared and Denby et al. [27] found r-squared of 28% when modelling PM10 in salt road emissions. P-value for NH₃ flow to the PT, mixer rotation and precipitation were over 0.05 so they are not considered significant by the criteria here applied and the model can be written as per Equation 2.

$$\text{ln (OSA)} = 16.69 + 0.007973 \text{ Liquor to PT} - 0.015599 \text{ Salts to PT} + 0.00323 \text{ Off-spec flow to PT} - 0.01627 \text{ Bucket rotation} + 0.000591 \text{ Liquor temperature} + 0.000762 \text{ Melt temperature} + 0.08369 \text{ Air temperature} + 0.00893 \text{ Wind speed} + 0.007250 \text{ RH\%}$$

(2)

The precipitation can be a contributor factor to relative humidity (RH%) which one was significant in the emissions model for OSA, but not on its own, probably because of its irregular distribution over the area, once the weather station is located 1.2km far from the stack monitored. Besides that, the year under analysis presented a dry summer with no precipitation, what can be interpreted in the model as a constant parameter. The same applies to NH₃ flow to the PT and the mixer rotation, once its little variation over time makes them not relevant for the model.

The transformation used to normalize the dataset when building the model seems to be adequate as can be seeing in Figure 6a, where the line is the model and the black triangles represent the residual when applying the model to the experimental results, if considered that this is an industrial application, not a controlled environment while the residuals presented a random distribution what led to conclude the OSA model has included most relevant parameters in the process, in the whole period, besides during fall and winter there is a trend to underestimate PM emissions. The residuals on Figure 6b appear to be higher than for EDA (Figure 5) but the magnitude order is different once for OSA the correlation to mg/Nm³ is about 0.3 times while for EDA is 5.45 times.

Winter is a challenge for the model as showed on Figure 6b once during this season there is a trend of underpredicting the emissions. This behavior could be due to the gases thermodynamic properties. In the area studied often negative temperatures are observed with low RH% and lower gas viscosity, leading the gas stream to have particles less agglomerated freely moving that could affect the sensor capacity to measure this very small UFPs considering that the wavelength of the optical sensor employed on OSA is 650nm.

The air temperature is by far the most significant parameter on the model, but here also the raw materials flow to the PT are showed as responsible for UFPs concentration showing that the optical sensor was able to measure this contribution. Gong et al. [28] states that optical scattering have developed enough to be applied on understanding UFP changes in the environment they are inserted and Mitchem and Reid [29] have studied the use of optical sensor to manipulate and characterize single particles in the range of 1 to 10µm.

![Figure 6. (a) Residuals versus model plot for OSA; (b) Model residuals for OSA over seasons.](image-url)
4 Conclusions

The best regression model found for EDA using transformed response was optimal lambda equal to -40 giving a r-squared equal to 9.49%, F-value of 53.91 (p-value of 0) and standard error of 2 mg/Nm$^3$. The most significant parameters in the EDA model were air temperature, RH% and precipitation, all meteorological parameters. The process parameters were at least one-degree order smaller than the meteorological ones.

On the other hand, the OSA model designed presented a standard error of 0.21mg/Nm$^3$ and r-squared of 45.25%, F-value of 425.32 (p-value of 0) equivalent to best models found in literature for ambient air application. The most relevant parameters in the OSA concentration model were

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