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Analysis of multivariate stochastic signals sampled by on-line particle analyzers: Application to the quantitative assessment of occupational exposure to NOAA in multisource industrial scenarios (MSIS)

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Abstract. In multisource industrial scenarios (MSIS) coexist NOAA generating activities with other productive sources of airborne particles, such as parallel processes of manufacturing or electrical and diesel machinery. A distinctive characteristic of MSIS is the spatially complex distribution of aerosol sources, as well as their potential differences in dynamics, due to the feasibility of multi-task configuration at a given time. Thus, the background signal is expected to challenge the aerosol analyzers at a probably wide range of concentrations and size distributions, depending of the multisource configuration at a given time. Monitoring and prediction by using statistical analysis of time series captured by on-line particle analyzers in industrial scenarios, have been proven to be feasible in predicting PNC evolution provided a given quality of net signals (difference between signal at source and background). However the analysis and modelling of non-consistent time series, influenced by low levels of SNR (Signal-Noise Ratio) could build a misleading basis for decision making. In this context, this work explores the use of stochastic models based on ARIMA methodology to monitor and predict exposure values (PNC). The study was carried out in a MSIS where an case study focused on the manufacture of perforated tablets of nano-TiO_2 by cold pressing was performed.

1. Introduction

As comprehensively reviewed by Kuhlbusch [12], different approaches have been used to obtain information about the exposure to NOAA: (a) Studies based on real workplaces and (b) process based studies in simulated workplaces and of simulated work processes. However, as they clearly pointed out, data about industrial processes working with nanomaterial products are still scarce [2,11,20] and the overview studies referred to herein give no clear results whether the actual nanomaterial was released or not. The increasing importance and use of NOAA in a diversity of industrial processes requires to build a consensus about both the determination of exposure scenaria and the specific needs in developing a method for the distinction of the background aerosol.

The currently widespread use of samplers and portable analyzers for continuous measurement of Particle Number Concentration (PNC) [5,6], the availability of strategies and measurement procedures [1,3,17,20], reference values (NRV) [18] and rules for decision [4], makes PNC a very suggestive metric for its use in the quantitative risk assessment of occupational exposure to airborne nanoobjects and their agglomerates and aggregates (NOAA). This metric is equally suggestive for monitoring industrial plants, to detect malfunctions and potential emergency situations in industrial processes manufacturing or handling manufactured nanomaterials or nano-enabled products. Furthermore, analysis and management of time series can be used to control exposure and operation in these industrial processes.

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However in all cases, the effective discrimination of the signal emitted by the sources with respect to the background is the main challenge of this approach [13,15,20], particularly in multisource industrial scenarios MSIS with high levels of background aerosol. A distinctive characteristic of these specific scenaria is the spatially complex distribution of aerosol sources, as well as their potential differences in dynamics, due to the feasibility of multi-task configuration at a given time. Thus, the background signal is expected to challenge the aerosol analyzers at a probably wide range of concentrations and size distributions, depending of the multisource configuration at a given time.

Measurement of PNC in workplaces differs from traditional sampling hygienic techniques because it requires the use of continuous devices - ELPI+, SMPS, CPC, OPS, Nanoscan, among other - which results in time series data, showing the evolution of the selected metric during the sampling time and whose length is proportional to the sampling frequency [5,6]. The comparability of the data provided by instruments based on different principles has been studied showing that divergence generally arose at the extremes of their working size range and at low number concentration. [16]. These differences were attributed to a response to the different operating procedures used by the instruments and/or the different particle types sampled. ELPI generally showed agreement with the SMPS, FMPS and APS, however this agreement is much poorer at the upper and lower ends of the ELPI working range. For the smallest particle size, the overall uncertainty is 20% (95 % confidence interval), decreasing towards larger sizes and levels at 40 nm particle diameter to 12 %. Regarding the TSI portable CPC 3007 the measurement accuracy specified by the manufacturer is ± 20 %.

The PNC nano reference value (NRV) for nanoTiO_2, defined as an 8 h time weighted average concentration adjusted for the background concentration, is 40.000 particles/cm^3 [18]. In addition, OELs mass based for nano TiO_2 (respirable fraction) have been proposed by NIOSH (0,3 mg/m^3) [12] and recently by project Scaffold (0,1 mg/m^3) [17].

At present, little attention has been paid on the statistical treatment of time series recorded by on-line analyzers of NOAA at workplaces. The analysis of metrics most commonly used, PNC and Particle Size Distribution (PSD), has been based on graphics and quantitative analyzes have been limited to the use of simple statistical parameters [7]. In signal processing and time series analysis there are numerous techniques in both time and frequency domains [8,19]. One of the most popular approaches are the stochastic ARIMA models. These models have been widely used in studies of air pollution, mainly for prediction. More recently ARIMA models have been applied to study time series collected by continuous aerosol analysers of NOAA, in order to identify the effect of a specific task on the concentration levels or to compare the level of concentration in repeated experiments [7]. In classical theory of Box-Jenkins [19], ARIMA models are listed using the standard notation of ARIMA (p,d,q)(P,D,Q), where p is the order of autoregression, d is the order of differencing (or integration), and q is the order of moving-average, and (P,D,Q) are their seasonal counterparts. These models have some limitations; they presume weak stationarity (Time series recorded by on-line analyzers of NOAA are rarely stationary), equal-spaced intervals of observations, no missing values and at least 30 to 50 observations. From stationary series, ARIMA methodology produces comprehensive models that not only explain the underlying generation process of the series themselves, but also can be exploited for further forecasting. In fact, these models may be further used to provide engineering feedback and design automated control systems in complex industrial scenaria.

In this context, this work focuses on exploring the applicability of PNC metric for quantitative assessment of exposure to nano TiO_2 in a MSIS. A second objective is aimed to know the background aerosol and its contribution to mask the effective discrimination of the signals at source. And finally, the ultimate goal is focused on the use of stochastic models based on ARIMA methodology to predict exposure values (PNC), based on the analysis of net signals (source minus background) obtained from raw time series recorded by continuous analyzers implemented in the MSIS.

2. Exposure scenarios

This study was carried out at the production plant of Bostlan SA, located in Mungia, (Spain). The company manufactures products for casting, among which alloying tablets and mini tablets for the aluminum industry, obtained by mixing and pressing metallic powders (Cr, Cu, Fe, Mn, Ni, Ti). All stages of the process (dosing, mixing, pressing, etc.) are controlled by computer, featuring a high degree of automation. In the framework of project EHS Advance [10], a case study focused on the manufacture of perforated tablets nano-TiO_2 was performed. Currently, Bostlan SA does not manufacture these products, so exposure scenarios lasted for a pilot batch of tablets (about two hours).

Figure 1. Layout and production lines of the company Bostlan SA. Inside the red circle, the exposure scenario 1 (EE1).

Measurements of TiO_2 were conducted in two exposure scenarios (Table 1): 1) Weighing TiO_2, 2) Production of TiO_2 tablets and 3) Finishing TiO_2 tablets. Positions 1 and 2 perform a single task (T1- Weighing or T2- Pressing) and are located in the production hall (Figure 1), where coexist with routine production of another type of tablets (EE1). WP3 is located in a separated room devoted to maintenance work (6 x 4 x 3 m), with two entrances (EE2). The four tasks described above involve the participation of two workers (W1 and W2). In EE1, W1 performs the weighing of TiO_2 (T1) and then W2 press the tablets (T2). After completion of T2 in EE1, W2 moves to EE2, to perform T3 and T4.

Table 1. Characteristics of exposure scenarios

Exposure scenario	Location	Workplaces	Tasks	Workers
EE1	Production hall	WP1. Weighing TiO_2 WP2. Production of TiO_2 tablets	T1. Weighing TiO_2 powder T2. Pressing TiO_2 powder	W1. Worker 1 W2. Worker 2
EE2	Maintenance room (6 x 4 x 3 m)	WP3. Finishing TiO_2 tablets	T3. Drilling tablets T4. Packaging tablets	W2. Worker 2

2.1. Exposure scenario 1 (EE1)

Task 1 - Weighing TiO_2 powder (T1). The amount of TiO_2 (powder) required for producing a tablet is manually weighed on an electronic scale. The TiO_2 loading on the weighing container, is done manually with a small shovel from the raw material bag (Figure 2). The operator W1 uses an average of about 50 seconds for each weighing. Exposure measurements were performed during 11 weighing of material. A pallet next to the workplace allows intermediate storage of the raw material bags.

Task 2– Pressing TiO_2 powder (T2). An automatic vertical axis manufacturing press was enabled in manual mode for the manufacture of tablets by pressing TiO_2. The press is located 3 m from WP1. The manual loading of TiO_2, press drive, machine manipulations during successive pressing cycles and the final manual removal of the tablet are performed by the same operator (W2) (Figure 2). Exposure measurements were performed during the manufacturing of 12 tablets. Each tablet requires between 2 and 4 minutes and several pressing cycles and intermediate manipulations. The press has a local exhaust ventilation system (suction speed of 0,23 m / s).

Figure 2. From left to right and top to bottom: 1) Weighing TiO_2 powder (T1); 2,3) Cold pressing of TiO_2 powder at vertical axis press (T2); 4) Resulting TiO_2 tablet at the end of machine cycle; 5) Drilling tablets (T3); 6) Packaging in lots of 5 tablets (T4).

2.2. Exposure scenario 2 (EE2)

Task 3 - Drilling tablets (T3). This task makes a hole in the center of the tablet using a vertical drilling. Each drilling operation requires approximately 10 to 20 seconds. Some tablets broke down during operation and then the worker (W2) cleaned the waste. Exposure measurements were made during drilling of 32 tablets.

Task 4. - Packaging tablets (T4). Once drilled, tablets are carefully wrapped with aluminized paper in packs of five and stored in box. Exposure measurements were carried out during the preparation of five packs of tablets.

2.3 Nanomaterial handled in exposure scenarios

The nanomaterial selected for the case study is nanoparticulate titanium dioxide manufactured by EVONIK, with Aerosil ® process (flame hydrolysis), under the trade name AEROXIDE ® TiO_2 P 25. According to MSDS provided by the manufacturer, this product is a highly dispersed titanium dioxide, with a crystallographic composition of 80% anatase and 20% rutile and an average primary particle diameter of 21 nm. However primary particles are not present in isolated form, but primarily as aggregates or agglomerates, and the average diameter of the resulting particles, typically is in the range of near-micron scale and well above 100 nm.

3. Measurement set-up and methodology

For the characterization both of background aerosols and aerosols at sources, direct measurement instrumentation was deployed (Table 2) by the case study. Instruments 1 to 4 were connected in rack, to ensure the simultaneous capture of aerosol in a fixed sampling point. A portable termohygrometer to monitor relative humidity and temperature during the measurements was placed at the sampling points of background aerosols, in EEI and EE2. Additionally a portable anemometer was used to monitor air currents and measure the capture speed of the local exhaust ventilation installed in the press. The measurement strategy followed the procedures provided by NANOGEM [1] that displays three hierarchical levels of evaluation. Operational constraints in Bostlan SA - it is a unique experimental lot of tablets scheduled for a particular day –, leads to the unfeasibility of repeated measurements. Thus, the tier 3 (expert evaluation) was directly deployed. Measurements were designed to provide tangible evidence of the presence or absence of TiO_2 in the atmosphere of the workplace, by combining advanced on-line instrumentation (Table 2) and off-line analysis of aerosol samples (SEM, ICP-MS, EDX, etc). The measurement strategy also included the determination of aerosol background by its simultaneous and continuous measurement in two selected locations.

This paper covers exclusively time series recorded by on-line instruments numbered as #1, #2 and #5 in Table 2. In both exposure scenarios, instruments #1 and #2 were dedicated to the registration of aerosol at source and #5 for registration of background aerosol. The selected metric in all cases was the PNC.

Table 2. Instrumentation deployed for on-line monitoring of aerosols at workplaces and instruments selected for the present paper (#1, #2 and #5).

Instrument and model		Metrics	Measuring range (nm)	Concentration range (#/cm^3)	Remarks
1	CPC (TSI 3775)*	Total particle number concentration	4 - > 3000	0 - 10^7	
2	ELPI+ (Dekati)*	Total particle number concentration and aerosol size distribution (channels)	6 - 10000	Depending on the most concentrated stage	These instruments shared a common sampling point
3	OPS (TSI 3330)	Total particle number concentration and size distribution	300 - 10000	0 - 3000	
4	Aerotrak 9000 (TSI)	Surface area of particles deposited in the lungs	10 -1000		
5	CPC (TSI 3007)*	Total particle number concentration	10 - 1000	0-10^5	Measurement of background aerosol

(*)Instrumentation selected for this paper

First, measurements in T1 were performed over a period of approximately 98 minutes, placing the sampling inlet next to the scale (40 cm). The following measurements were performed for 50 minutes in T2, positioning the inlet, 40 cm from the axis of the press. While performing these tasks, the instrument that measured the background aerosol was located about 8 meters of the working area. After finishing T1 and T2, the rack of instrumentation moved to EE2. In this room T3 and T4 were performed. In both cases, the sampling inlet was located at a distance of about 30 cm from the sources. While performing these tasks, background concentration was measured on the opposite side of the room, about 6 m from T3 and 3 m from T4. In all cases the sampling inlet was positioned closed to the breathing zone of workers W1 and W2.

Statistical analysis of time series was performed with the statistical package SPSS 22.0. This software includes a time series modeler allowing to build custom non seasonal or seasonal ARIMA models for time series, with or without a fixed set of predictor variables, and producing forecasts. The module includes also an expert modeler that automatically identifies and estimates the best-fitting ARIMA model for one or more dependent variable series. Both conventional trial-error and expert modeler approaches were combined in this study.

4. Time series and modelling

4.1 Time series recorded in EE1

At EE1, the measurement log includes a first period without tasks named Period of Inactivity 1 (POI1). This period can be divided into two sections: POI1.1 preceding the start of the industrial activity in plant and POI1.2 in which all production processes are running. During period POI1, the rack of instrumentation was positioned at the location of T1. During the whole measurement period (POI+ T1 + T2), the ELPI+ measured significantly higher levels of particles than the other instruments (Figure 3). PNC raw signals provided by equipment at source evolve approximately in parallel with a continuous offset of 15.000 #/cm^3 between both signals. Both paths have several very marked relative maxima, the two most important are symmetric (110/120.000 #/cm^3) and recorded during POI2. Minimum values of PNC, around 25.000 #/cm^3, were recorded at the beginning of the measurement, when industrial plant processes had not begun to operate yet (POI1). PNC at source before starting T1, recorded during the POI2 under MSIS conditions, can be considered, for all purposes, as background concentrations during this period. The amplitude of maximum values (up to 120000 #/cm^3) provides a clear picture of the strong influence exerted by the background aerosol during tasks T1 and T2.

Table 3. Percentage of PNC with an aerodynamic diameter less than 100 nm, 380 nm and 1000 nm in time series (from data provided by ELPI +

Task	≤100 nm	≤380 nm	≤1000 nm
T1 - Weighting	92,85	99,85	99,96
T2 - Pressing	91,43	99,83	99,95
T3 - Drilling	86,81	99,85	99,96
T4 - Packaging	84,10	99,78	99,94

If we separate the whole PNC signal recorded by the ELPI+ during T2 into two size ranges, "small particles" (≤ 1µm) and "large particles" (> 1µm) (Figure 3), it has been shown that the first signal replicates perfectly the whole signal, both in morphology and amplitude, including almost all of the aerosol particles. The second signal presents a smoothing path on which are several peaks, with maximum at about 176 #/cm3, coinciding temporally with the completion of tasks T1 (2724 data) and T2 (2727 data) and with no significant reflection in the total signal.

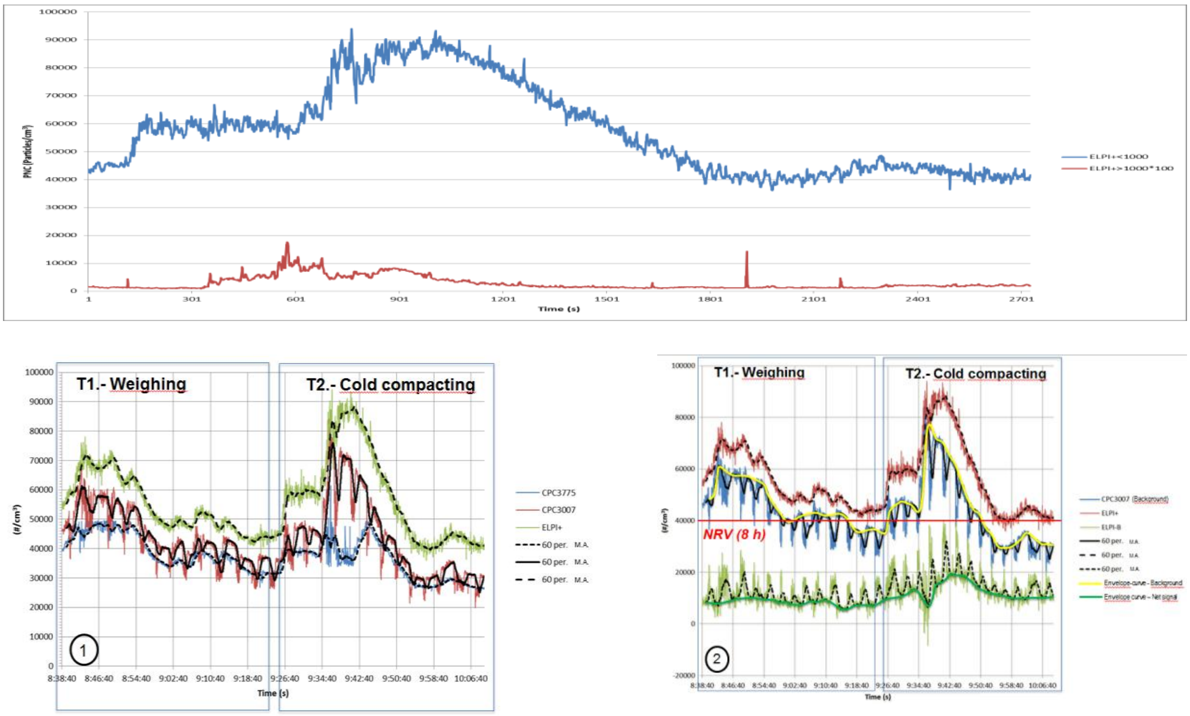

Figure 3. Top; PNC time series recorded by ELPI + during T2 showing the contribution of submicron and supermicron particles to the aerosol. 1) Raw time series captured at source and bakground during T1 and T2; 2) Net signal time series (source minus background) and its smoothed envelope (in green).

The measurement of background aerosol at EE1 begins during the completion of T1. If a section of this record is segmented and analyzed in detail, it appears that the general trend is altered by a set of periodic oscillations (Figures 3.1). During T1 and T2, reasonable agreement was noted between the signal measured at source and the smoothed background envelope calculated from CPC 3007 raw data, once the influence of the periodic signal has been suppressed. The offset between the two signals oscillates around 10.000 -15.000 #/cm^3. However during pressing (T2), these signals are significantly separated, presenting opposite evolutions which increase the offset until 60.000 #/cm^3. With respect to the pulsating component recorded by the background analyzer, it was initially attributed to the impact of manufacturing processes and mobile diesel machinery present in the production hall. However, after analyzing the industrial process in detail, the results point to a spurious component of the aerosol analyzer signal due to non-damped vibrations at the measurement point.

4.2 Time series recorded in EE2

Data recording started before T3&T4 (Figure 4), as denoted by POI2, period of inactivity 2. During POI2 the measuring rack was placed at the sampling point T3. Satisfactory agreement was reached between signals from different instruments. PNC raw data provided by equipment at source evolve in parallel, with an offset of about 7000 and 12000 #/cm^3. ELPI+ plot shows an increasing steepness from around 32000 #/cm^3 up to 54000 #/cm^3 and then a gradual decreasing to values of PNC below obtained at the beginning of the measurement (4000 #/cm^3). The background PNC shows a general agreement with the above mentioned signals recorded at source, a significant noise component in the ascending segment of the graph and, a maximum of 44000 # /cm^3. Data measured before beginning T3 can be considered as values of background aerosol. None of the three recorded PNC signals (source and background), appears influenced by potential releases during tasks T3 (2661 data) and T4 (1491 data).

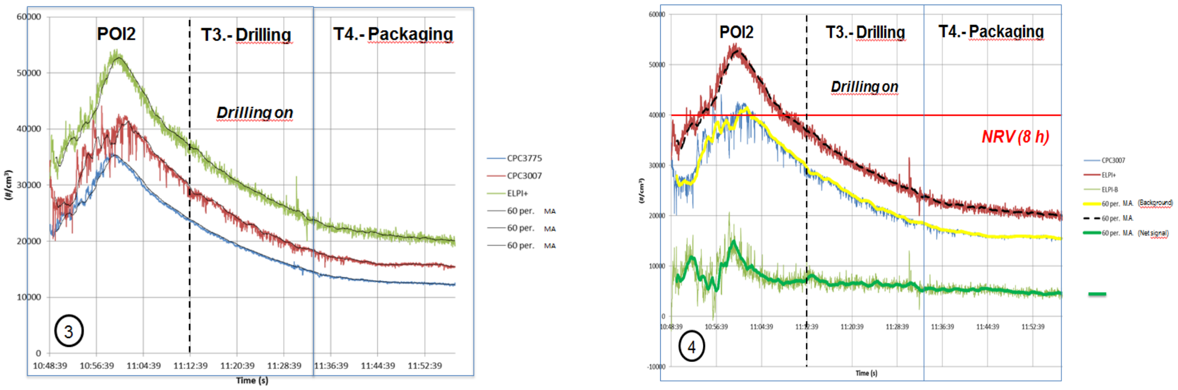

Figure 4. From left to right: 3) Raw time series captured at source and background during T3 and T4; 2) Net signal time series (source minus background), (in green).

4.3 Time series of net signals

Net signals were calculated by subtracting the background from the signal at source and initially were supposed to represent the contribution of NOAA releases to PNC from tasks (Figure 4a, 4b).

In EE1 the resulting temporal profile of net PNC during T1 and T2 also shows a serrated profile, shaped by the raw background signal (Figure 3.2). The smoothed net signal envelope exhibits during T2, a clear maximum around 38000 #/cm3. Its offset with respect to the corresponding maximum of the background, could suggest a contribution of NOAA released to the PNC. Nevertheless, this cannot conclusively confirmed due to the high level of background aerosol concentration. In this context, the resulting signals obtained for T1 and T2 cannot be directly interpreted as the net contribution of potential releases to the workplace PNC, since these signals may combine in a indistinguishable way the true NOAA releases, the effects of the different instrumental response between the collocated analyzers at source, the increase in the concentration of the background aerosol or a combination of all three.

In EE2, the net PNC signal obtained for T3 and T4 (Figure 4.4) exhibits significant peaks before starting T3 (drilling). The rest of the signal is damped on a level approximately constant at around 7000 # /cm^3 - corresponding to the difference of amplitude between the raw signals - without significant contributions of tasks evaluated.

Table 4. Summary statistics of time series for PNC

Time Serie	Sampling period	N	Instrument	Max	Min	P25	Mdn	P75	Range	Mean	s	CV
T1 Weighing	8:38:40 9:24:03 (45’ 23’ ‘)	2724	CPC 3775	49660	26800	34610,0	37970,0	45707,5	22860,0	39376,6	5843,8	14,8
			CPC 3007	69095	26286	37447,0	42304,0	51453,3	42809,0	44118,4	8652,6	19,6
			ELPI+	78049	38051	47326,3	51049,0	62993,8	39998,0	54533,3	9238,2	16,9
			Net signal	28676	2075	7745,3	9405,0	12393,5	26601,0	10414,9	3932,7	37,8
T2 Pressing	9:24:04 10:09:30 (45´26’ ‘)	2727	CPC3775	61480	25470	28370,0	35130,0	39600,0	36010,0	34987,5	6583,3	18,8
			CPC 3007	84167	19854	31077,0	38031,0	48736,0	64313,0	42499,9	13776,3	32,4
			ELPI+	94068	35974	43184,0	56315,0	66998,0	58094,0	57448,6	15786,2	27,5
			Net signal	39806	576	10891,0	13991,0	17816,0	39230,0	15037,9	5848,3	38,9
T3 Drilling	10:48:39 11:32:59 (44´ 20’’)	2661	CPC 3775	35750	13990	18630,0	23680,0	28295,0	21760,0	23915,0	6019,3	25,2
			CPC 3007	44113	17495	23090,5	28013,0	35311,5	26618,0	29141,1	6977,7	23,9
			ELPI+	54214	20045	29639,0	36396,0	42353,5	34169,0	36748,5	8245,2	22,4
			Net signal	20775	344	6142,3	6937,0	8506,3	20431,0	7631,6	2466,6	32,3
T4 Packaging	11:33:00 11:57:50 (22`50’’)	1491	CPC 3775	14770	11950	12520,0	12769,0	13340,0	2820,0	12965,4	595,6	4,6
			CPC 3007	18582	14864	15795,0	15988,0	16760,0	3718,0	16309,6	750,0	4,6
			ELPI+	25117	19006	20523,0	21193,0	22079,0	6111,0	21365,2	1086,8	5,1
			Net signal	8325	3413	4606,0	5037,0	5445,0	4912,0	5055,6	617,8	12,2

4.3 Time series modelling

In the case of the net PNC signal along T1 & T2, the operational problems described above, hinder their further modelling. Thus, the following discussion about time series modelling will refer to the net PNC along tasks T3 and T4.

Table 5 summarizes the ARIMA models evaluated to model time series T3 (2661 data) and T3&T4 (4152 data). As shown in Figure 4 both series were not stationary, so we proceeded to differentiate once the original series (d), obtaining in both cases resulting stationary series. Then, from the graphs of autocorrelation and partial autocorrelation functions (ACF and PACF), p and q parameters of the regular models (without seasonal component) were estimated. The models initially identified were the ARIMA (1,1,2) for T3 and ARIMA (2,1,1) for T3&T4. In both cases the models were over fitted - increasing by one unit the parameters p and q - and new models were tested to verify if they provided a better fit. The model initially selected for T3 (1,1,2) was also tested for T3&T4. All models included a constant in the initial estimation, which was suppressed in all cases, because it was not significantly different from zero. The models were recalculated again without constant. The ARIMA (2,1,2) model was removed from the final selection for both time series, because several model parameters showed no significant coefficients.

Table 5. Summary of models parameters and the goodness of fit of the models predictions (no significant coefficients between brackets; in bold, the two models finally selected).

Time serie	Model ARIMA	Constant	AR1	AR2	D	MA1	MA2	R^2	RMSE	MAPE	MaxPE	BIC	Ljung-Box
T3 (2661)	**(1,1,2)**	[1,990]	**0,568**	**-**	**1**	**0,552**	**0,251**	**0,890**	**831,655**	**9,196**	**745,177**	**23,459**	**Indepen.**
	(2,1,1)	[2,325]	0,780	-0,228	1	0,768	-	0,890	831,184	9,165	671,516	13,457	Indepen.
	(2,1,2)	[2,079]	0,612	[-0,052]	1	0,594	0,198	0,890	831,896	9,197	732,753	13,462	Indepen.
T3&4 (4152)	(1,1,2)	[0,862]	0,599	-	1	0,602	0,233	0,912	705,470	8,075	822,586	13,124	Indepen.
	(2,1,1)	**[1,104]**	**0,794**	**-0,218**	**1**	**0,798**	**-**	**0,912**	**705,418**	**8,049**	**728,790**	**13,124**	**Indepen.**
	(2,1,2)	[1,032]	0,700	[-0,124]	1	0,700	[0,108]	0,912	705,394	8,063	766,609	13,128	Indepen.

Normalized BIC criterion (Bayesian Information Criterion) was used among the remaining four models to select the best-fitting model and more parsimonious, with auxiliary criteria for goodness of fit R^2, RMSE, MAPE and MaxPE. The Ljung-Box criterion was used to demonstrate the independence of residuals (significant in all cases). At the end of the process the ARIMA (1,1,2) for T3 and (2,1,1) for T3&T4 were selected, although both models provide substantially similar fitting. In figure 5 the goodness of fit of model ARIMA (2,1,1) is shown for a representative section of time series T3&T4.

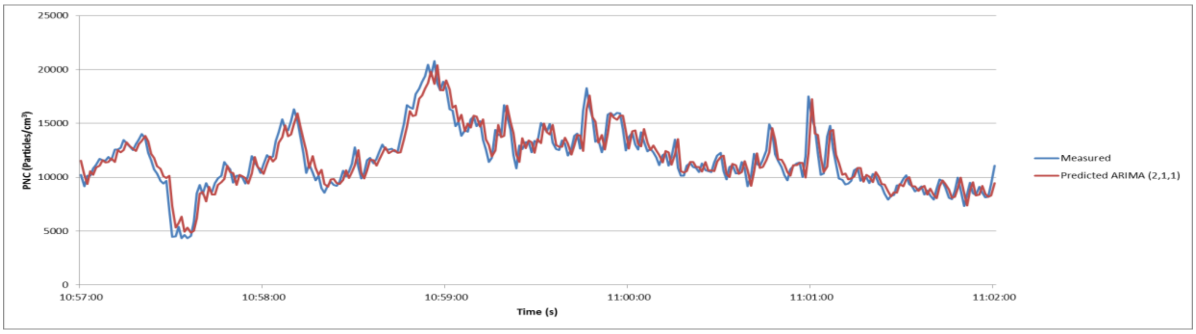

Figure 5. Fit between PNC measured in T3&T4 and predicted using a model ARIMA (2,1,1).

5 Conclusion

PNC method applicability to MSIS. The PNC is insensitive to emissions in the super-micron range, so depending on the type of NOAA will be roughly performant and/or distinguishable from the background. If the background is high, the typical state of the art aerosol analyzers offset can lead to accuracy problems or even masking between the source and the background signals. In MSIS, dynamic background is a critical element especially when going to average and can induce BIAS on averaging. The net signal can be conditioned by physical artifacts (equipment malfunction, high levels of background) that should be identified and filtered prior to mathematical treatment. In these cases, subtraction of 8 h time weighted average concentrations may result in uncertainty in the assessment of exposure value which is then compared with the NRV. This does not mean that in terms of background stable, the PNC method may be applicable in similar terms to those already demonstrated in other industrial environments (e.g. such as stationary processes, labs).

Background signal distinction in real time and time integrated. When there is a dynamic background as demonstrated above, subtraction of 8 h time weighted averages may lack physical meaning and its comparison with the NRV have no sense. During tasks T1 to T4, net concentration calculated during the sampling time presents values always below the NRV proposed for nanoTiO_2 (40.000 particles/cm^3) (Table 4). However fluctuations of PNC in the aerosol at source are not linked to emissions during the evaluated tasks but are caused by changes in the background, related to manufacturing processes operation, diesel transport machinery, etc. Consequently the comparison between the net value of PNC and corresponding NRV has no physical meaning and therefore their application is not appropriate.

Statistical analysis of time series of PNC has been proven to be feasible in predicting PNC evolution provided a given quality of net signals [7]. However the analysis of non-consistent time series could build a misleading basis for decision making.

There is a need for more experimental studies in real MSIS, which could help to refine the procedures for the assessment of occupational exposure to NOAA, according to the well-established tiered approaches. The challenges are closely related to the distinction of the dynamic background. In this sense a promising approach currently under exploration might be the use of SNR parameter (Signal-to-Noise Ratio) for discriminating whether the MSIS pattern allows the applicability of the evaluation approach based on PNC.

The exposure assessment in company Bostlan SA was solved using mass as metric and applying the NIOSH method. The values 8h averaged, were far from OEL established by NIOSH (0,3 mg/m^3). In addition, SEM microscopy confirmed the evidence of nanoTiO_2 agglomerates in the breathing zone of workers during T1 to T4, whose size ranged from approximately 5-10 µm [10].

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