Estimating airborne heavy metal concentrations in Dunkerque (Northern France)

Germán Santos[1*], Ignacio Fernández-Olmo[1], Ángel Irabien[1], Frédéric Ledoux[2], Dominique Courcot[2]

[1]Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Santander, 39005, Spain

[2]Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV) EA 4492, Université du Littoral Côte d'Opale, Dunkerque, 59140, France

[*]Corresponding author. Tel.: +34 942201579; fax: +34 942201591

E-mail address: santosg@unican.es

Abstract

This work aims to estimate the levels of lead (Pb), nickel (Ni), manganese (Mn), vanadium (V) and chromium (Cr) corresponding to a three-month PM_{10} sampling campaign conducted in 2008 in the city of Dunkerque (Northern France) by means of statistical models based on Partial Least Squares Regression (PLSR), Artificial Neural Networks (ANN) and Principal Component Analysis (PCA) coupled with ANN. According to the European Air Quality Directives, because the levels of these pollutants are sufficiently below the European Union (EU) limit/target values and other air quality guidelines, they may be used for air quality assessment purposes as an alternative to experimental measurements. An external validation of the models has been conducted, and the results indicate that PLSR and ANNs, with comparable performance, provide adequate mean concentration estimations for Pb, Ni, Mn and V, fulfilling the EU uncertainty requirements for objective estimation techniques, although ANNs seem to present better generalization ability. However, in accordance with the European regulation, both techniques can be considered acceptable air quality assessment tools for heavy metals in the studied area. Furthermore, the application of factor analysis prior to ANNs did not yield any improvements in the performance of the ANNs.

Keywords: harbour town; immission levels; PM10; heavy metals; statistical models (PLSR, ANN)

1. **Introduction**

Recent studies have shown a positive correlation between high concentrations of particles and public health deterioration. Particulate Matter (PM) remains a concerning environmental problem in urban areas due to its physical properties, such as mass distribution, particle size and shape, and chemical composition, which may include various acidic and toxic species such as metals, metalloids and aromatic compounds (Karar and Gupta 2006). In addition to industrial emissions, non-exhaust PM emissions from road traffic have been identified as an important source of metals in urban environments (Thorpe and Harrison 2008). Furthermore, long-term exposure to metals could cause severe toxic effects on human health (Chen and Lippmann 2009).

In this context, the European Union, through the Air Quality Framework Directive (EC 2008) and the 4th Daughter Directive (EC 2004), has established a set of air quality objectives for certain pollutants in PM_{10}: a limit value of 500 ng m^{-3} for Pb (Directive 2008/50/EC) and target values of 6 ng m^{-3} for As, 20 ng m^{-3} for Ni and 5 ng m^{-3} for Cd (Directive 2004/107/EC) for the total content in the PM_{10} fraction averaged over a calendar year. Along with these limit/target values, an upper and lower assessment threshold (hereafter known as UAT and LAT) are also specified, expressed as a percentage of the corresponding limit/target value as follows: 70 and 50 % (Pb and Ni) and 60 and 40 % (As and Cd). Depending on the level of pollutants with respect to these thresholds, different air quality assessment methods with respect to the pollutants are permitted. Thus, in accordance with Directive 2008/50/EC, when the pollutant levels are below the lower assessment threshold (LAT), the air quality may be assessed using solely modelling or objective estimation techniques without the need for experimental measurements. Taking into account the high cost and time consumption associated with analytical determination of the levels of these pollutants, it may be interesting to try to find new alternatives for air quality assessment so that fewer experimental measurements may be required.

According to the Guidance on Assessment under the EU Air Quality Directives, “objective estimation technique” is a fairly broad term that includes mathematical methods to calculate concentrations from values measured at other locations and/or times based on scientific knowledge of the concentration distribution. Empirical data-based modelling or statistical modelling falls within this definition and represents an attractive alternative to deterministic modelling (air dispersion modelling), given that it requires less specific knowledge of the system under consideration as it attempts to find the existing relationship between the immission concentrations of pollutants and other variables that may influence the processes that control the formation, transportation and removal of aerosols in the atmosphere, disregarding the physical principles in which the equations that describe these processes are based on, as well as other decisive information such as emission inventories.

Partial Least Squares Regression and Artificial Neural Networks have been proposed in this study to estimate PM_{10}-bound heavy metals because both have been used in the literature as mathematical techniques to forecast the air concentration of a number of pollutants. Pires et al. (2008), Polat and Durduran (2012) and Singh et al. (2012) applied PLSR to predict PM concentrations, and numerous authors over the years have investigated the development of ANN models to predict PM concentrations and gaseous pollutants (Gardner and Dorling 1999; Kukkonen et al. 2003; Perez and Reyes 2002), to cite but a few. Furthermore, Chelani et al. (2002) performed not only a prediction of PM_{10} concentration but also of ambient air metal levels, namely Cd, Cr, Fe, Ni, Pb and Zn, with a low prediction error. Moreover, because the number of independent input variables is relatively high with respect to the number of samples, an alternative approach based on applying Principal Component Analysis (PCA) prior to ANN development was considered due to this technique being reported in the literature as an effective strategy to improve model performance (Lu et al. 2003, Sousa et al. 2007, Ul-Saufie et al. 2013).

Despite having a relatively small contribution to the total content of PM in terms of mass, metals in Dunkerque have been reported as clear tracers of the local industrial activities in the city (Kfoury 2013). In this respect, the main objective of this work is to estimate the levels of some EU-regulated and non-regulated metals in airborne PM_{10} in the urban area of Dunkerque. For this purpose, statistical models based on PLSR and ANNs have been developed as objective estimation techniques.

It is worth mentioning that because this work is devised as an air quality assessment tool at a later stage, it is about estimation instead of forecasting. Thus, it is intended to provide an estimation of the pollutant concentrations of the recent past as an alternative to experimental measurements instead of predicting future pollutant concentrations.

2. Description of the methodology and area of investigation

2.1 Partial least squares regression fundamentals

Partial least squares regression is a statistical method that, as with other multivariate regression techniques, seeks to find the relationship between two data matrices in order to predict a response or a set of response variables (*Y*) from a set of predictors (*X*). However, it differs from other multivariate calibration techniques in that it aims to reach two goals simultaneously as follows: to capture variance and to achieve correlations, i.e., maximize covariance (Abdi 2010). That is to say, PLSR attempts to find factors that maximize the amount of variation explained in X that is relevant for predicting Y as a generalization of other related techniques, e.g., principal component regression (PCR), which obtains factors based solely on the amount of variance captured in X and disregards entirely the covariance, and multiple linear regression (MLR), which tries to find a single factor that best correlates predictors with responses.

By performing a projection of the original predictor variables into a new space, PLSR creates a set of orthogonal factors, referred to as *latent variables*, to be used to predict the output variable(s). This projection is performed as follows: first, the X-matrix is decomposed as a product of a set of X-scores T multiplied by a set of X-loadings P.

$$X = TP' + E \tag{1}$$

X-scores are expressed as a linear combination of the original predictor variables by means of a set of vectors of coefficients known as *weights*, which ensure the orthogonality of scores.

$$T = XW^* \tag{2}$$

where

$$W^* = W(P'W)^{-1} \tag{3}$$

In parallel, a similar decomposition is performed for the Y-matrix, which is expressed as a product of the Y-scores U multiplied by the Y-loadings C.

$$Y = UC' + G \tag{4}$$

As mentioned before, X-scores not only model X (Eq. (1)) but also predict Y. This prediction is achieved using Eq. (5).

$$Y = TC' + F = XW^*C' + F = XB + F \tag{5}$$

Therefore

$$B = W^*C' \tag{6}$$

Further details of this technique can be found in Wold (2001). PLS Toolbox (Eigenvector Research, Inc.) for MATLAB was used in the present study to develop the PLSR models.

2.2 Artificial neural network fundamentals

Artificial neural networks are computational systems based on biological nervous systems that attempt to mimic the fault-tolerance and capacity to learn of biological neural systems. They are formed by a number of highly interconnected simple processing elements, or artificial neurons (also known as nodes or units), receiving a set of inputs, either from original data or from the output of other neurons in the neural network, via weighted connections (or weights) that resemble synaptic connections in a biological neuron. These nodes are arranged into three types of layers, i.e., input, hidden and output layers. Data are fed into the nodes in the input layer and later transferred to the subsequent layers. Every node in the hidden and output layers also has a single bias value known as the activation threshold value. Being the weighted sum of the inputs computed, the corresponding threshold value is subtracted to compose the activation of the neuron. The activation signal is passed through an activation function (also known as a transfer function) to produce the output of the node. The relationship between the output and the inputs finally has the mathematical representation, as presented in Eq. (7):

$$y_t = w_0 + \sum_{j=1}^{q} w_j . g\left(w_{0,j} + \sum_{i=1}^{p} w_{i,j} x_{t,i}\right) + \varepsilon_t \quad (7)$$

where p is the number of input nodes, q is the number of hidden nodes, $w_{i,j}$ $(i = 0,1,2, \dots, p, j = 1,2, \dots, q)$ and w_j $(j = 0,1,2, \dots, q)$ are connection weights, and ε_t is a bias error.

A multitude of neural network architectures are possible. However, in practice, simple network structures with a relatively small number of hidden nodes often work well in out-of-sample forecasting. In this work, a multilayer perceptron (MLP) neural network with a sigmoid hidden transfer function and a linear output transfer function has been selected, applying the Levenberg-Marquardt learning algorithm. A schematic representation of the network structure is shown in Fig. 1.

The ANN models in this study were developed using the Neural Network Toolbox for MATLAB (MathWorks, Inc.).

2.3 Description of the area of study and sampling site

The city of Dunkerque, with a population of approximately 68,000 inhabitants in 2008, is located on the northern coastline of France, limited by the French-Belgian border. The main urban area is surrounded in its northern part by the harbour of Dunkerque, which is classified as the third most important port in France due to shipping and freight transport (including ore, coal and copper, among other goods) and as the seventh port in order of importance of Northern Europe. The city is also in close proximity to the English Channel, connecting the North Sea with the Atlantic Ocean, which is the world's busiest seaway, with approximately 500 vessels transiting daily. There is also a highly industrialized area in the city's vicinity for the metallurgic industry, as it has an integrated steel manufacturing plant (nearly 4 km NW), an electric steel plant (6 km NE) and a ferromanganese alloy production plant (at approximately 6 km W).

A total of 78 samples were measured throughout an *intensive* PM_{10} sampling campaign performed from February to May 2008 in Dunkerque by Hleis (2010). Fig. 2 shows the location of the sampling site (51º02’07’’N, 02º22’05’’E and approximately 10 m above sea level), which was placed on the rooftop of the Les Darses site (to prevent the sampling of punctual events at street / ground level) on the boundary line between the industrial area and the city so that the effects of both urban and industrial emissions were registered during sampling (under WSW and NNW wind sectors) (Kfoury 2013). Further details of the sampling procedure are described in Hleis (2010). The composition of inorganic elements (Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sn, Ti, V and Zn) and ions (Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) in the particles was determined. The mean values of these constituents are reported in Hleis (2010).

2.4. Modelling database and pre-treatment

As usual for this type of modelling, input variables consist of (i) meteorological data, namely average temperature (ºC), average relative humidity (%), prevailing wind direction (º), prevailing wind speed (ms^{-1}), average pressure (mbar) and cumulative precipitation (L m^{-2}), which are obtained at the meteorological station in the harbour of Dunkerque, and (ii) major pollutant data, which are composed by average concentrations (µg m^{-3}) of sulphur dioxide (SO_2), tropospheric ozone (O_3) and nitrogen oxides (NO_x) measured at the St. Pol sur Mer air quality monitoring station (the Atmo-Nord-Pas-de-Calais air quality network) and PM_{10} concentrations measured at the Les Darses site. Additionally, two nominal variables were considered to account for the seasonal (1: Winter, 2: Spring, 3: Summer, 4: Fall) and weekend effects (0: Working day, 1: Weekend).

Output variables in this study consisted of PM_{10}-bound Pb, Ni, Mn, V and Cr levels in ambient air (ng m^{-3}) at the sampling site. Among the EU regulated metals, Pb and Ni were determined. Additionally, three non-regulated metals were also considered: Mn, V and Cr. These metals were tracers of various industrial activities found in Dunkerque, where previous studies on trace metal levels have been developed: Mn, for ferromanganese alloys manufacturing; V, for marine traffic and liquid fuel combustion; and Cr, for non-integrated steel manufacturing and coal combustion (Kfoury 2013). Because these metals are not regulated by the EU, they do not have a limit/target. Therefore, to normalize the metal concentration and calculate the EU uncertainty indices, the following values were considered as equivalent to the LAT for non-regulated metals: the annual air quality guideline for Mn (150 ng m^{-3}) proposed by the World Health Organization (WHO 2000) and the maximum observed concentration for V and Cr in the absence of a standard value for a period of duration comparable with that of the period of study.

As shown in Fig. 3, the Pb and Ni mean values are below their respective LAT. Therefore, according to the EU Air Quality Directives, objective estimation techniques can be applied for the air quality assessment in relation to Pb and Ni.

A pre-treatment procedure for outlier identification and removal based on the statistical parameter of the Mahalanobis distance was conducted. Additionally, as usual for this type of technique, the complete database was divided into three subsets as a result of applying a data-splitting procedure, the Kennard-Stone algorithm, which selects the more representative samples for each subset based on Euclidean distances. Thus, 60 % of the total number of samples was used for model development, 20 % for verification to avoid over-fitting and 20 % for external validation. Furthermore, to avoid scale effects, the dependent variables were normalized by dividing the metal concentrations by their respective LAT.

2.5 Model performance criteria

In this study, the evaluation criteria to determine whether a model is suitable for air quality assessment purposes is principally based on the following: (i) the fulfilment of the European Union uncertainty requirements for objective estimation techniques, and (ii) the accuracy of estimated mean values because the metal limit/target values correspond to annual mean concentrations. Two indices of uncertainty were calculated: the relative maximum error without timing (RME) and the relative directive error (RDE). The former is the largest concentration difference of all percentile (*p*) differences normalized by the respective measured value (Borrego et al. 2008), as calculated by Eq. (8). The latter is the difference between the closest observed concentration to the limit/target value and the correspondingly ranked modelled concentration normalized by the limit/target value (Denby et al. 2010), as given by Eq. (9).

$$\mathrm{RME} = \max\left(\left|C_{O,p} - C_{E,p}\right|\right) / C_{O,p} \qquad (8)$$

$$\mathrm{RDE} = \left|C_{O,LV} - C_{E,LV}\right| / LV \qquad (9)$$

Additionally, a number of statistical parameters were considered to evaluate the model performance. These performance indicators are the fractional bias (FB), the correlation coefficient (*r*), the root mean squared error (RMSE) and the fractional variance (FV), as given by Eqs. (10-13):

$$r = \left[\frac{\sum_{i=1}^{n}\left(C_{O,i} - \overline{C_O}\right)\left(C_{E,i} - \overline{C_E}\right)}{\sqrt{\sigma_O \sigma_E}}\right] \qquad (10)$$

$$FB = \frac{\overline{C_O} - \overline{C_E}}{0.5\,(\overline{C_O} + \overline{C_E})} \quad (11)$$

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(C_{O,i} - C_{E,i}\right)^2} \quad (12)$$

$$FV = 2\,\frac{\sigma_O - \sigma_E}{\sigma_O + \sigma_E} \quad (13)$$

where n = the total number of observations, $C_{O,i}$ = the ith observed value, $C_{E,i}$ = the ith estimated value and $\overline{C_O}$ and $\overline{C_E}$ are the observation and estimation averages, respectively. These indicators were calculated in both development and validation steps.

3. Results and discussion

3.1. Levels of the studied metals

Fig. 3 shows that the Pb and Ni mean concentrations for the period of study are below the corresponding legislated objective/limit values for ambient air. Moreover, the Mn average concentration is also below the WHO air quality guideline in relation to manganese. Nevertheless, there are some particular cases, i.e., Ni and Mn, where the non-averaged concentrations (individual sample concentrations) of these pollutants amply exceed the corresponding objective/limit values as follows: as shown, the Ni and Mn maximum observed concentrations exceed by 10 and 6 times their LAT and LAT-equivalent values, respectively. Special attention should be paid to model performance in this sense because exposures to high levels of these metals may have detrimental effects on human health. It has been demonstrated that inhaled manganese produces neurotoxic effects that vary from neuropsychological and motor functions (Mergler et al. 1999), postural stability (Hernández-Bonilla et al. 2011) and increased risk of Parkinson's disease (Finkelsteinn and Jerret 2007) at lower concentration exposures (near 50 ng m^{-3}) to a movement disorder known as Manganism at concentrations above 1 mg m^{-3} (Aschner et al. 2005). Regarding vanadium, its toxic effects depend on its degree of oxidation and may include irritation of the respiratory tract, haematological and biochemical changes and functional lesions in certain organs (Sumanta et al. 2015).

The studies conducted by Hleis (2010) and Kfoury (2013) have shown that the levels of Pb, Ni, Mn, V, Cr and other metals and metalloids in Dunkerque are remarkably associated with industry as they have been reported to be tracers of local industrial activities. The results of pollution roses and receptor modelling for source apportionment by means of non-negative matrix factorization indicate that Pb emissions may be mainly attributed to integrated steelworks, which is an Mn emission source as well (Kfoury 2013; Hleis 2010). However, the ferromanganese manufacturing plant emissions also influence the levels of Pb and certainly the levels of Mn (Hleis 2010). Ni and V are tracers of heavy oil combustion because they explain

72 % and 86 % of the observed concentrations, respectively (Kfoury 2013). With regard to Cr, it is considered to be a marker of the activity of the electric steel plant, although Cr levels may also be partly due to oil combustion. The strong presence of industrial activities in Dunkerque and the firm connection between ambient air metal levels and the local industry makes the city a suitable location to develop objective estimation models for metals because the inputs to these models partly consist of major pollutant concentrations, which are undoubtedly related to industry as well.

3.2. Estimation of Pb and Ni

Table 1 presents the results obtained with the best developed models for the two considered EU-regulated metals (Pb and Ni) using the three different considered approaches as follows: PLSR, ANNs and PCA-ANN. Results related to training (T) and external validation (V) subsets are presented for each model.

In the first place, for the evaluation of these models as an air quality assessment tool from a regulatory point of view, which is the main goal of the present study, the mean value estimation and the conformity of the compliance with the uncertainty requirements are two key aspects to take into account. In this regard, while complying with the uncertainty requirements (expressed in this study in terms of the RME and RDE indices) because both uncertainty indices are well below 100 %, which is the maximum uncertainty percentage allowed by the EU for objective estimation techniques to be used for air quality assessment, every model is able to provide a good estimate of the mean concentration due to the lower values obtained for the FB index, which is an indicative measure of the accuracy in estimating mean values. For the training stage, the PLSR FB index values are lower than the FB values with ANNs and the PCA-ANN model. The reason why the FB index of PLSR models is so small is that the PLSR-estimated and observed mean values are nearly equal, resulting in an FB index very close to its ideal value, which, according to Eq. (11), is 0. However, if attention is to be paid to the values of the rest of the FB indices, it is evident that they are not significantly higher as the estimated mean values are close to the corresponding observed values in every case.

It is worth noting that the mean values in this work are not in fact annual mean concentrations because the available data samples belonged to a period of study limited to three months, from mid-February to mid-May 2008. The sampling period varied from 6 to 14 hours, and consequently, the levels of pollutants presented significant variability. Therefore, there was an additional difficulty for the estimation.

Although a correct estimation of the mean value while fulfilling the EU uncertainty requirements is sufficient for a model application in the frame of the EU Air Quality Directive, it would be greatly preferable for the model to also be able to correctly estimate the individual sample concentrations. To evaluate this capacity and provide a more comprehensive response of model performances, a series of additional statistical indicators have been addressed. With regard to these performance indices, the correlation coefficient values of the PLSR and ANN models are within the range of 0.5-0.9, indicating a good tendency of the estimated and observed values to vary together. Nevertheless, even if the *r* values are close to 1, there is no guarantee that the estimated and observed values match each other, only that they may differ by a consistent factor. For this reason, other statistics must be taken into consideration.

As for PCA-ANN models, they provide lower values of the correlation coefficient - within the range of 0.3-0.6- than PLSR and ANNs. This fact, together with an increase in uncertainty indices, indicates that, for this specific application, performing PCA prior to the development of ANNs is not an effective alternative.

Models have been evaluated on the basis of comparisons against observations via a set of statistical indicators, which, while providing insight on general model performance, do not necessarily indicate whether model results have reached a sufficient quality level for a given application, e.g., for policy support. Ideally, models should have a correlation coefficient close to 1 and FB, RMSE and FV values close to 0. Unfortunately, in practice, due to the uncertainty of observation and the analytical determination in the laboratory, these values will rarely be achieved. In this regard, Kumar et al. (1993) propose values for some of these parameters associated with a minimum quality for the models: NMSE $\leq$ 0.5 and -0.5 $\leq$ FB $\leq$ 0.5.

A supplementary manner to evaluate model performance is by means of a graphic representation. In this regard, Fig. 4 depicts the estimated normalized concentrations of Pb and Ni obtained with the PLSR and ANN models for the training and external validation subsets. As observed, both models exhibit difficulties in accurately estimating the individual sample concentrations, leading to an underestimation of the highest concentrations. Notwithstanding, PLSR and ANNs capture the underlying trend during training, although there is a slightly better fitting when using ANNs, as reflected in the lower RMSE and FV values obtained with ANNs with respect to those obtained with the PLSR model.

With respect to the external validation subset, as a result of a decrease in the accuracy of the estimations, there is a general slight decrease in the correlation coefficient values and an increase in the values of the RMSE and FV indices of every model compared with those obtained for the training subset. However, the FB index values for PLSR and ANNs are below 0.5 and, therefore, within the acceptable range for FB for an air quality model suggested by Kumar et al. (1993). Additionally, for the PLSR and ANN models, the correlation coefficient of the external validation subset ranged from 0.5-0.8, which was similar to those obtained for the training subset. Consequently, based on the performance results obtained for external validation, PLSR and ANNs may be considered proper approaches to estimate ambient Pb and Ni levels in the studied site. Nevertheless, as a general remark, the best pair of training and external validation statistics are found when using ANNs, which indicates that the model is able to not only fit the data correctly but also provide good estimates of data not used for the development of the models, which implies that ANNs present better generalization ability than the other studied techniques.

3.3. Estimation of Mn, V and Cr

The results of the best developed models for Mn, V and Cr are presented in Table 2. Despite the fact that the ambient air levels of these pollutants are not regulated by the European Directives, the model evaluation analysis is performed in the same manner as in the case of Pb and Ni. Nevertheless, because these pollutants are lacking a policy limit/target value, an RDE-equivalent (RDE_{eq}) uncertainty index has been calculated based on the version equivalent to LAT values for regulated pollutants, as mentioned in section 2.4. Note that, with this assumption, Mn, V and Cr mean values, unlike those of Pb and Ni, are closer to their corresponding LAT.

As can be observed, the EU uncertainty requirements for objective estimation techniques are fulfilled with an RME and an RDE_{eq} lower than 100 % in all cases, except for the external validation RME index of the Cr PCA-ANN model. However, it could be argued that because some of these metals may present considerably higher air concentrations, such as Mn, which exceeds by almost six times 150 ng m^{-3} (which is the WHO air quality guideline used as LAT-equivalent) with a maximum observed value of 872.8 ng m^{-3} for the period of study (Fig. 3), more restrictive uncertainty requirements should be addressed, considering that an allowed 100 % uncertainty in the estimation may lead to erroneously regarding as acceptable an underestimation of a potentially dangerous pollutant level.

With respect to the mean concentration, lower values of the FB index for the Mn, V and Cr PSLR and ANN models indicate acceptable training and external validation estimations. These values are within the same order of magnitude as those obtained for Pb and Ni and below 0.5, complying with the minimum quality requirements proposed by Kumar et al. (1993). Again, that is not applicable to Cr PCA-ANN models with an external validation FB index of -1.46.

As for the models' performance in relation to the estimation of individual sample concentrations, correlation coefficient values lower than 0.66 for external validation indicate an unsatisfactory fitting.

However, this measure can be dominated by a small proportion of extreme values that may not reflect the behaviour of the bulk of the data. At any rate, the ANN model correlation coefficients are greater than those obtained for the PLSR and PCA-ANN models. This, together with the fact that ANNs provide the lowest FB index and adequate RME and RDE_{eq}, points to ANNs as the most suitable approach of the three studied.

4. Conclusions

In this work, statistical models based on PLSR and ANNs to estimate the levels of the considered EU-regulated metals, i.e., Pb and Ni, have been developed and externally validated. Based on the results obtained and according to the European Air Quality Framework Directive, these models can be taken into consideration as valid approaches to be used as objective estimation techniques for air quality assessment in relation to metals in the area of study because they are able to correctly estimate mean values within an uncertainty range up to 100 %. Both linear (PLSR) and non-linear (ANNs) statistical models show a comparable performance, although the latter exhibit an enhanced generalization ability. However, ANN performance experienced no improvements by the application of factor analysis techniques, such as PCA, before model development.

Additionally, in this study, some metals that lack a limit/target value in European legislation, namely Mn, V and Cr, have also been considered due to the strong relationship that exists between their levels and the local industry of the study area and due to the scientific evidence that suggests that some of these non-regulated metals can also cause damage to human health. As with Pb and Ni, the PLSR and ANN models for Mn and V work relatively well in terms of mean estimation within the EU Directive uncertainty limits. Nevertheless, they are not able to properly describe variations of Cr.

Finally, the statistical models developed for every metal struggle with the estimation of the individual sample concentrations and, as with many deterministic models, tend towards a slight underestimation. Therefore, further work will focus on deepening knowledge regarding the interactions between the different inputs and their relationship with the outputs to improve this specific matter.

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Figure captions

Figure 1: Structure of the artificial neural network

Figure 2: Sampling site and monitoring and meteorological stations in Dunkerque

Figure 3: Box-plot of the levels of Pb, Ni, Mn, V and Cr for the period of study. The box extends between the upper and lower quartiles with the inner line representing the median value. The whiskers indicate the minimum and maximum values.

Figure 4: Comparison between the observed and modelled normalized Pb and Ni concentrations

Table 1

Table 1. Uncertainty, mean concentration and performance statistics for the best models developed for Pb and Ni

Metal	**Model**	**Subset**[a]	**EU Uncertainty**		**Mean Concentration**[b]			**Performance**		
			RME (%)	**RDE (%)**	**C_O 10^2**	**C_E 10^2**	**FB 10^2**	**r**	**RMSE 10^2**	**FV 10**
Pb	PLSR	T	28.1	1.44	6.52	6.52	3.7 10^{-08}	0.823	3.94	1.95
		V	31.9	0.31	7.46	8.88	-17.4	0.837	4.48	-2.78
	ANN	T	18.3	2.10	6.38	6.84	-7.0	0.932	2.72	-0.85
		V	54.0	0.54	7.46	8.31	-10.8	0.861	4.90	-4.12
	PCA-ANN	T	40.1	2.22	6.57	6.78	-3.2	0.663	3.90	5.82
		V	90.4	1.38	3.69	7.95	-73.1	0.266	5.64	-2.56
Ni	PLSR	T	65.9	12.87	68.5	68.5	-7.5$10^{-11}$	0.560	80.5	5.64
		V	83.6	11.70	156.6	98.2	45.8	0.556	241.3	14.62
	ANN	T	29.2	18.55	73.4	73.8	-0.5	0.873	54.2	1.44
		V	50.0	17.60	156.6	115.8	30.0	0.702	186.6	4.77
	PCA-ANN	T	64.9	24.86	95.9	95.8	0.1	0.470	161.1	7.20
		V	42.6	2.50	68.6	94.9	-32.2	0.443	63.2	-3.04

[a] T: Training; V: Validation

[b] O: Observed; E: Estimated

Table 2

Table 2. Uncertainty, mean value and performance statistics for the best models developed for Mn, V and Cr

Metal	Model	Subset[a]	EU Uncertainty		Mean Concentration[b]			Performance		
			RME (%)	RDE_{eq} (%)	C_O 10^2	C_E 10^2	FB 10^2	r	RMSE 10^2	FV 10
Mn	PLSR	T	53.9	4.71	32.55	33.43	-2.7	0.580	41.49	3.57
		V	53.1	50.23	64.95	58.24	10.9	0.184	92.80	6.99
	ANN	T	52.6	60.51	33.61	21.38	44.5	0.704	39.20	3.42
		V	48.2	68.86	64.95	63.77	1.8	0.457	81.56	4.64
	PCA-ANN	T	66.4	78.51	46.05	46.05	0.0	0.463	64.77	7.34
		V	35.3	11.62	29.49	30.33	-2.8	0.431	42.72	1.74
V	PLSR	T	42.7	1.20	13.12	13.42	-2.3	0.694	8.17	2.33
		V	31.5	4.74	18.07	18.48	-2.2	0.590	11.21	3.16
	ANN	T	41.6	4.28	14.27	14.00	1.9	0.806	7.19	1.78
		V	30.7	5.45	18.07	18.45	-2.1	0.663	10.43	2.11
	PCA-ANN	T	42.9	1.60	13.14	13.20	-0.5	0.747	5.91	2.93
		V	12.5	15.60	12.79	16.50	-25.4	0.366	13.97	0.56
Cr	PLSR	T	88.8	1.01	4.58	3.96	14.6	-0.031	15.28	11.34
		V	78.5	25.74	6.97	5.78	18.7	0.077	18.09	12.78
	ANN	T	50.0	39.17	5.59	3.25	53.1	-0.040	19.24	6.53
		V	83.6	27.89	6.97	3.55	65.0	-0.240	19.06	14.76
	PCA-ANN	T	79.2	0.43	7.15	7.90	-10.0	0.331	18.33	9.70
		V	489.9	0.43	1.45	9.31	-146.3	0.275	10.04	-13.57

[a] T: Training; V: Validation

[b] O: Observed; E: Estimated

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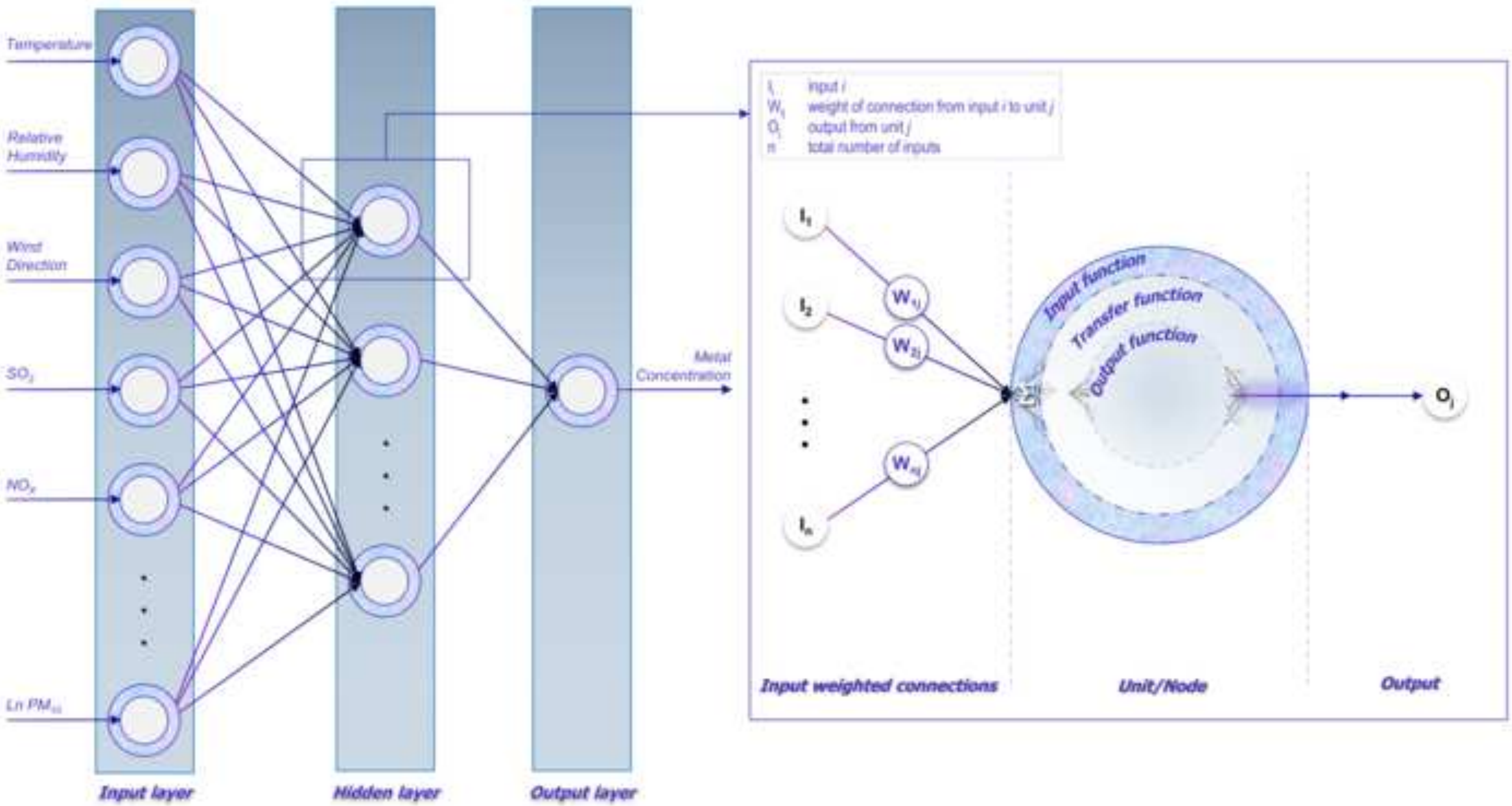

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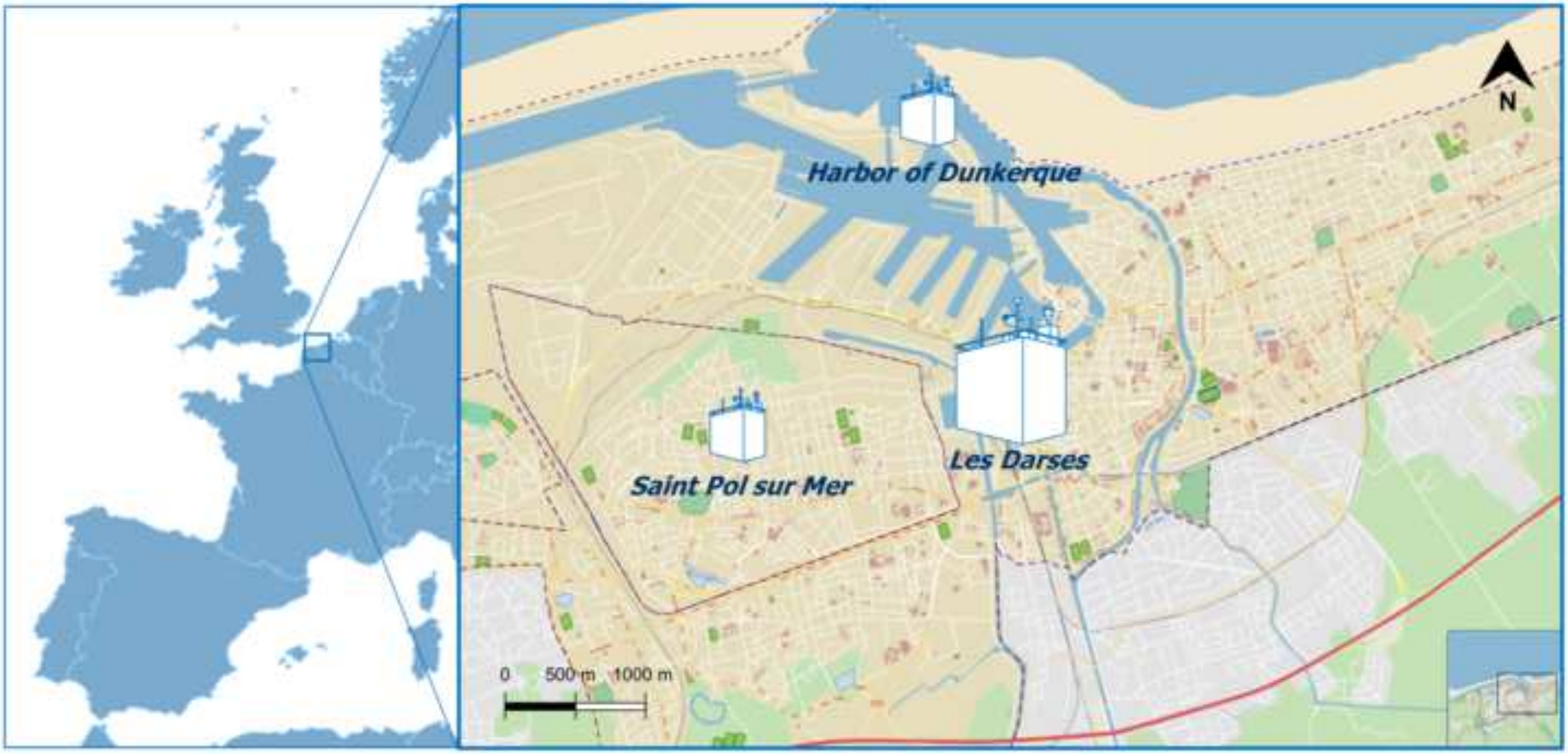

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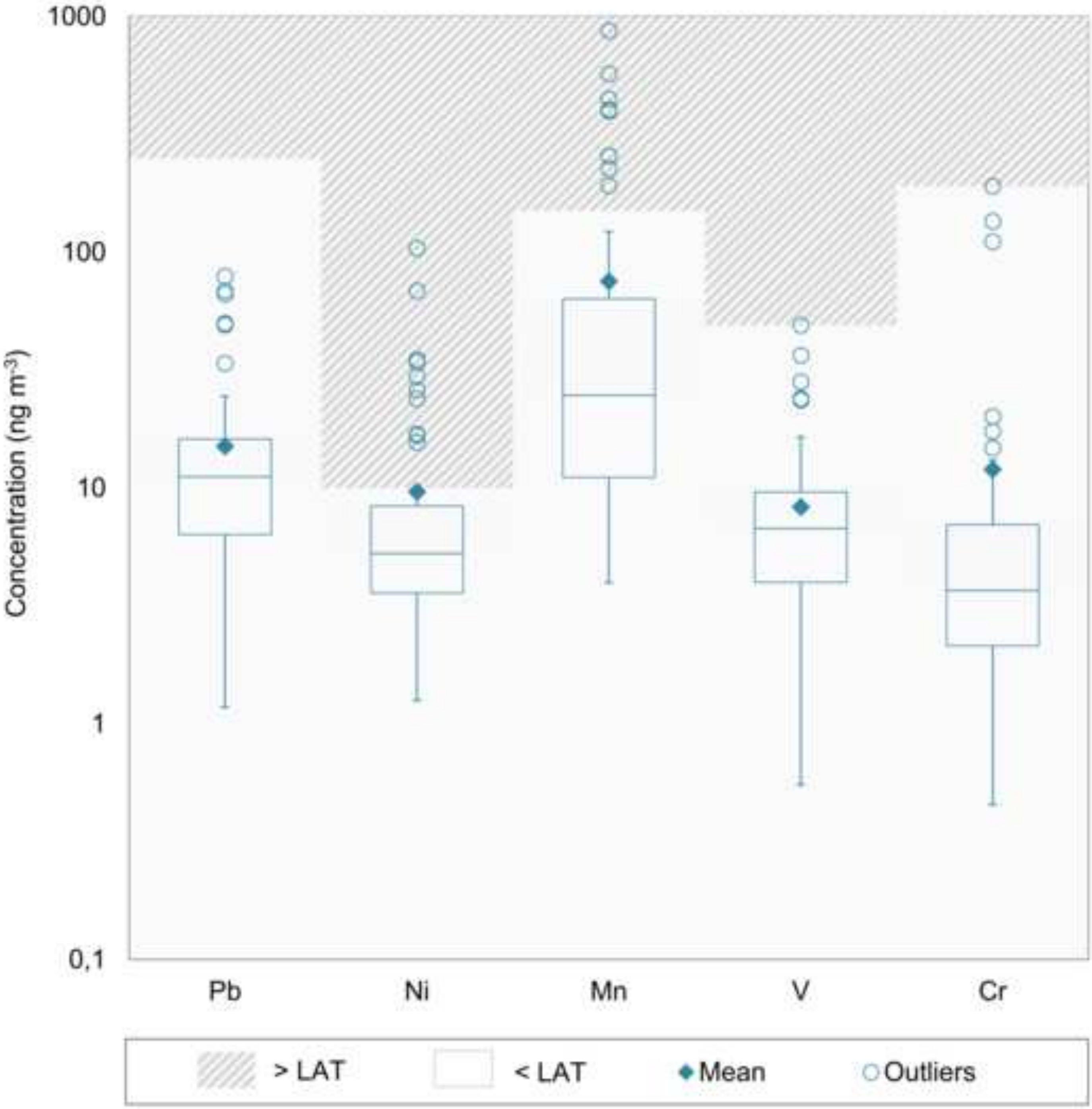

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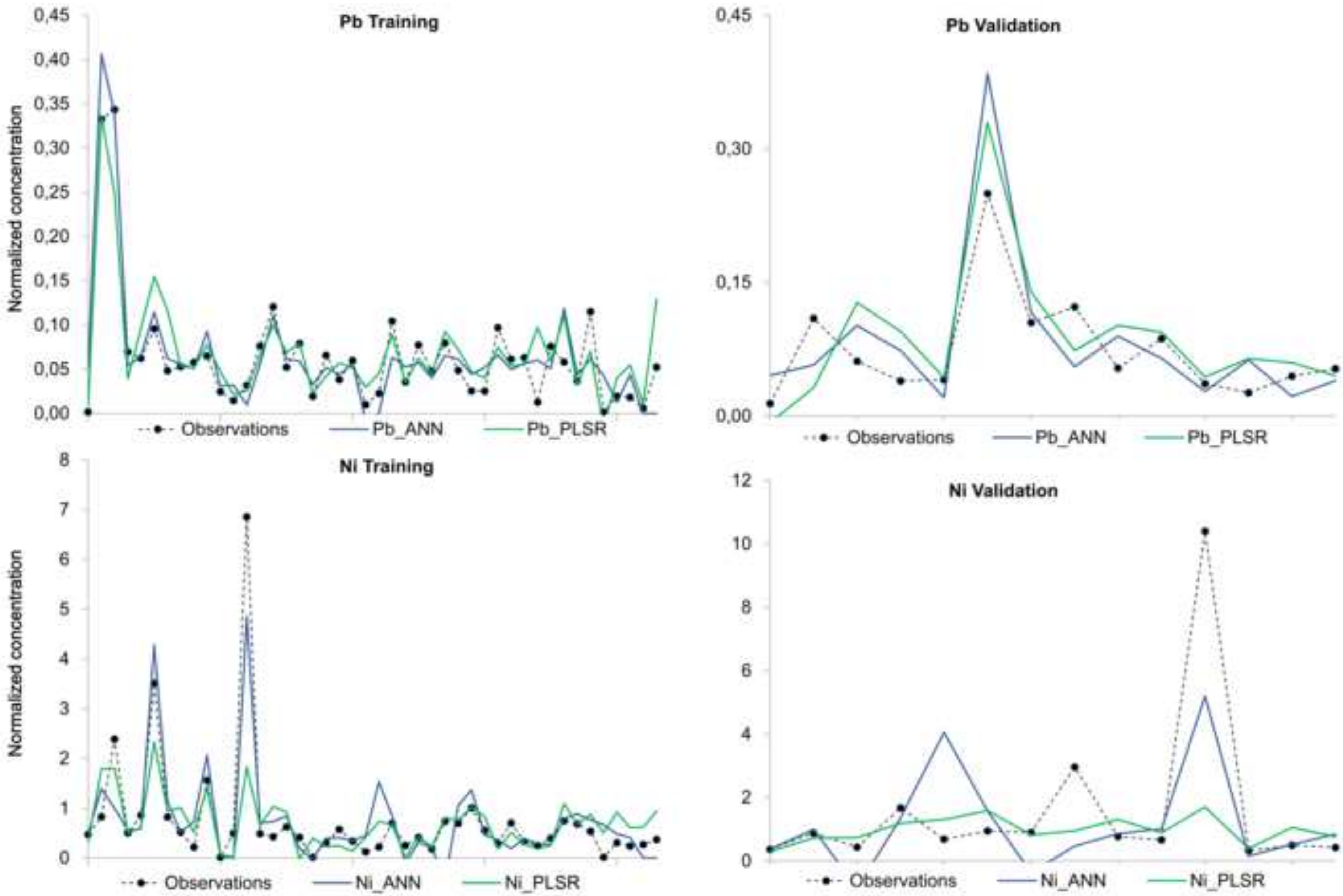

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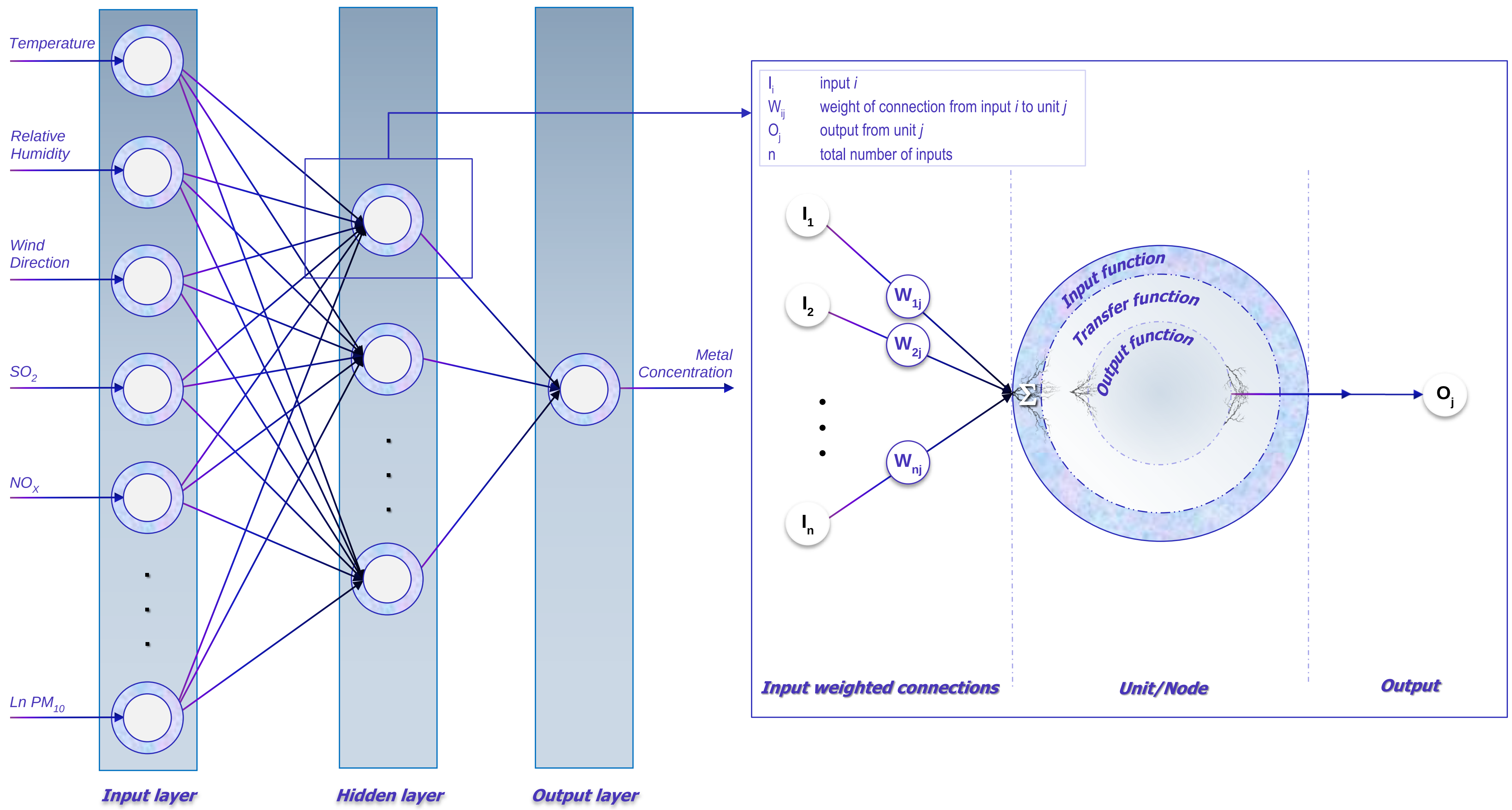

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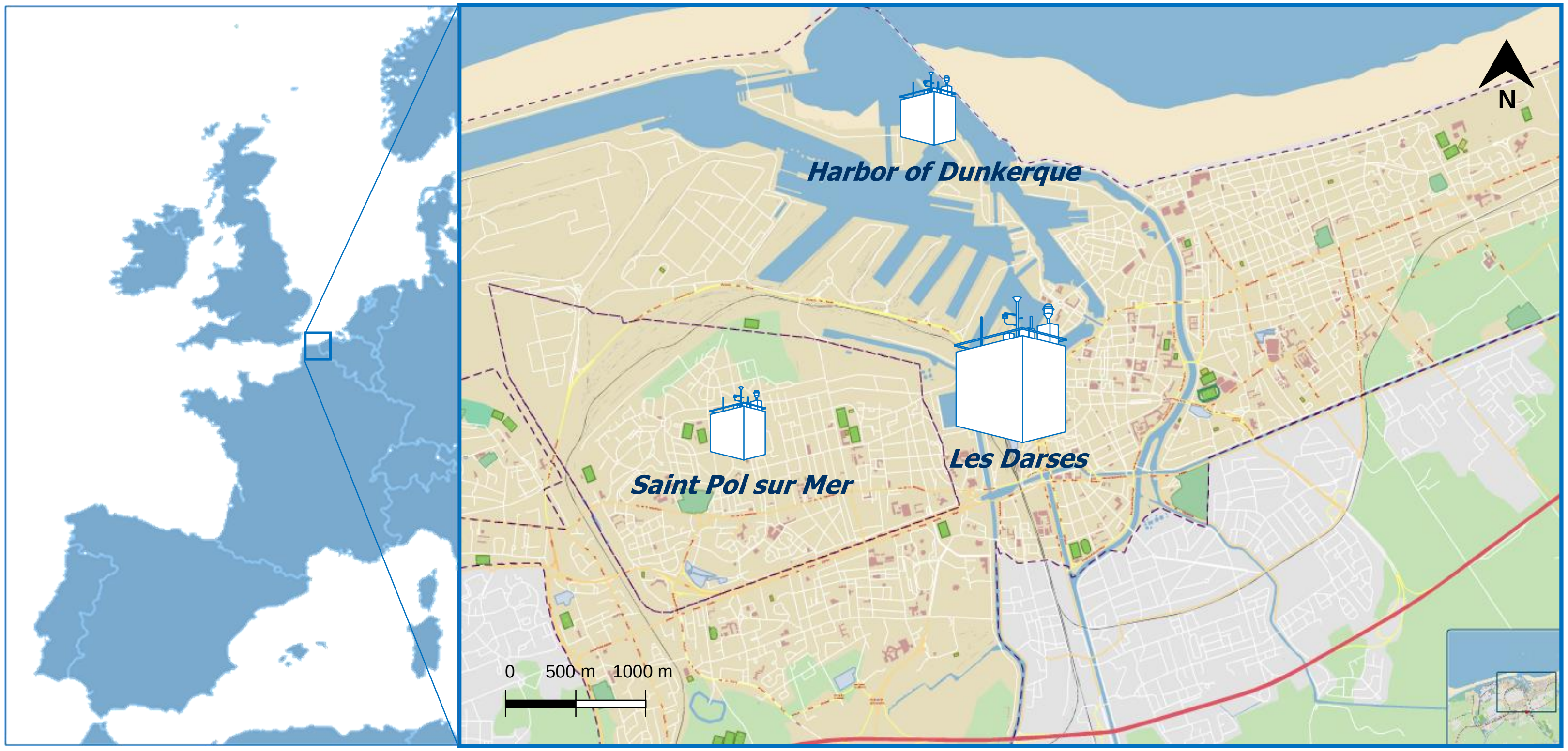

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