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Abstract

Ammonia levels were evaluated in the urban environment of Madrid City, Spain. A total of 110 samplers were distributed throughout the city. Vehicle traffic density, garbage containers and sewers were identified as local emission sources of ammonia. The average ammonia concentrations were 4.66 ± 2.14 $\mu g/m^3$ (0.39-11.23 $\mu g/m^3$ range) in the winter and 5.30 ± 1.81 $\mu g/m^3$ (2.33-11.08 $\mu g/m^3$ range) in the summer. Spatial and seasonal variations of ammonia levels were evaluated. Hotspots were located in the South and Center of Madrid City in both winter and summer seasons, with lower ammonia concentrations were located in the North (winter), West and East (summer). The number of representative points that were needed to establish a reliable air quality monitoring network for ammonia was determined using a combined clustering and kriging approach. The results indicated that 40 samplers were sufficient to provide a reliable estimate for Madrid City.

Keywords Ammonia levels, diffusive samplers, screening method, air quality network

Ammonia is a primary air pollutant emitted from different sources (natural and anthropogenic) to the atmosphere. It plays a very important role in the atmospheric chemistry, participating in atmospheric deposition processes and reacting with other gases (Bittman et al. 2015) to form particulate matter such as ammonium salts (Zheng et al. 2015). Therefore, changes in ammonia concentrations may modify particle concentrations (Malm et al. 2013). Ammonium salts can be harmful to human health (Webb et al. 2014).

Many researchers have used diffusive samplers to carry out screening studies (Pienaar et al. 2015), to map air pollutants and identify hotspots (Hien et al. 2014). However, this methodology has not been used to evaluate the minimum number of representative sampling points needed to assess the air pollutants in an urban environment. In this work, an air quality monitoring network for ammonia was designed to assess the ammonia levels in an urban environment. Air quality data from an air quality monitoring network is important for the development of monitoring strategies (Mofarrah and Husain 2010) and for assisting authorities in making decisions. On the one hand, the network should consist of a sufficient number of sampling points to provide information on spatial variation of atmospheric pollutants in the studied area (Zheng et al. 2011). Equally, the network must not duplicate information on air pollutants (Losada et al. 2014). Consequently, the design of air quality monitoring networks is an important factor for the protection of human health from air pollutants (Pope and Wu 2014).

The Municipality of Madrid has worked to reduce the emissions of total ammonia (http://www.madrid.es). These efforts have focused on emissions from road transport and waste treatment. Total ammonia emissions in Madrid City decreased from 1868 tons in 2006 to 689 tons in 2014. The objectives of the present study were to evaluate the spatial and seasonal variations for ammonia concentrations in the air of Madrid City, to identify local emission sources, and to determine the minimum number of representative sampling points needed to establish an air quality network for ammonia in an urban environment.

Materials and Methods

This work has been conducted in Madrid City. It has over 3,000,000 inhabitants and a surface of approximately 600 km^2 (Instituto Geográfico Nacional 2013, www.ign.es). It is located in the center of the Iberian Peninsula and divided into 21 districts and 128 neighborhoods. The studied domain was established based on the population density of the different neighborhoods. The peripheral neighborhoods with a population density below 50 inhabitants/hectares were removed from the study domain (Fig. 1).

Diffusive samplers (Radiello, Fondazione Salvatore Maugeri, PD, IT, described at http:www.radeillo.com) were used to carry out the sampling process (reference codes: 168 and 120-1 for Radiello cartridge and sampler, respectively). The samplers were placed at a height of approximately 2.5 m above the ground, and were covered with protective shelters in order to protect the samplers from the effects of meteorological conditions, such as wind and precipitation. The samplers contained cartridges impregnated with phosphoric acid (Wongniramaikul 2012). Ammonia is adsorbed in these cartridges as ammonium ion (Frati et al. 2007). Ammonium ion salts, as particulate matter, do not cross the diffusive membrane of sampler. The diffusive samplers are based on the Fick's First Law (Poddubny and Yushketova, 2013). This Law postulates a phenomenon of mass transfer through a layer of gas or a membrane. It is based on a process of concentration gradient. It relates the flow of gas that diffuses from regions of high concentration to regions of low concentration with the exposure time and the area of the passive sampler. The sampling rate value used in this study was 235 ml/min at 298 K and 1013 hPa. The sampling period was set for one week and two sampling campaigns were conducted (winter campaign: from 19-26 November 2014 and summer campaign: from 1-8 July 2015).

A total of 110 sites were sampled. Samplers were placed on a 1000 by 1000 meter grid. A total of 7 samplers were used for assessing the relationship between ammonia levels and traffic density during the studied periods. Traffic density data was donated by the Municipality of Madrid. Twenty samplers were placed up to 30 m of distance from garbage containers, and 14 samplers were placed at distances up to 7 m from sewers in order to identify local possible emission sources. It is necessary to be noted that these emission sources were variable from site to site based on factors such as neighborhood population density and urbanistic development, therefore, the ammonia emission sources (garbage containers and sewers) were not identical at all sampling sites. One garbage container and one sewer was sampled in each sampling point. The diffusive samplers located closer to the garbage containers and sewers were placed on street light poles in the vicinity of roadways (2.5 m above levels ground). These sites were characterized by a low traffic density (< 15,000 vehicles/day). Therefore, the major local emission sources in these sites were considered to be the garbage containers and sewers.

Following the sampling process, the cartridges were extracted by ultrasound in 5 ml deionized water and analyzed for ammonium ion by the indophenol blue method (Tatari et al. 2017) and ultraviolet-visible spectrophotometry at λ=635 nm. Calibration curves ranging in concentrations of ammonium ion from 0.5-5.0 µg/mL were regarded as acceptable only with coefficients of determination ≥ 0.999. An ammonium chloride standard (Fluka reference 59755; 1,000 ± 5 µg/mL) diluted to concentrations of 0.5, 1.5, 3 and 4.5 µg/mL served as quality control standards. The criteria for acceptance of these control standards was measured concentrations that were ≤ 10% of the known concentrations. The ammonia concentrations in ambient air were calculated based on the analyzed ammonium mass, sampling rate and sampling time.

Statistical clustering analysis of the data was conducted by IBM SPSS Statistic v22. Ammonia iso-concentration maps and the geostatistical estimation process were developed using ArcGIS v10.2.2. The geostatistical estimation method used to carry out the spatial interpolation of the obtained data was the Kriging method. Kriging is explained by Woodard et al. (2010) and Lin et al. (2012). This interpolation method provides unbiased information about values at non-sampled sites with a minimum estimated variance (Baume et al. 2011).

Formation of k-means cluster was conducted in order to minimize the number of representative sampling points to establish an air quality monitoring network in Madrid City. On the other hand, Euclidian distance as spatial indicator (Shahraiyni et al. 2015) and the cluster standard deviation as cluster membership identifier were used to form the k-means cluster. The k-mean algorithm is a partitioning method used in the clustering (formation of groups of similar objects). This algorithm looks for a fixed number of clusters which are defined in terms of proximity of data points to each other according to the Euclidean distance (Berry and dan Linoff 2004). In this work, ammonia data were grouped using an iterative process that began with the random assignment of a cluster to each data point. Subsequently, data were rearranged within the clusters by assigning them to the nearest cluster centre (Javadi et al. 2017).

Euclidean distance measurement is based on homology search approach (Ghosh and Barman 2016). The k-means cluster and Euclidean distance method were explained by Singh et al. (2013) and Kusrini (2015). The goal of this approach was to determine the minimum number of samplers that would be required to obtain reliable ammonia concentration data for the City of Madrid.

Results and Discussion

A statistical summary of obtained results and meteorological information is shown in table 1. Climatological data were obtained from a meteorological station placed in Barajas (Madrid, 40º27'00.06'' N 3º33'00.01'W). The prevailing wind direction was mainly toward the SW. The average ammonia concentration was 4.66 ± 2.14 µg/m^3 (0.39-11.23 µg/m^3 range) in the winter, and 5.30 ± 1.81 µg/m^3 (2.33-11.08 µg/m^3 range) in the summer. These concentrations are well below levels that are known to affect human health.

The World Health Organization has established that exposure to ammonia concentrations in ambient air of 280 mg/m^3 can produce irritation of the throat, of 1,200 mg/m^3 can produce cough, of 1,700 mg/m^3 can be dangerous for life and above 3,500 mg/m^3 can cause high mortality (WHO 1986. The iso-concentrations maps of ammonia in Madrid City are shown in Fig. 2. Hotspots were located in the South and Center of the city in both seasons, with lower ammonia concentrations being measured in the North (winter), West and East (summer). The City design and meteorological conditions may partially explain the distribution of ammonia levels in Madrid City.

The average ammonia concentrations were higher in summer than in winter due to the ambient temperature which plays an important role in the gas-phase ammonia/ammonium salts equilibrium. Formation of ammonium nitrate does not occur at temperatures > 25 ºC (Adams et al. 1999). Therefore, the conditions are not favourable for the formation of ammonium nitrate in summer. On the other hand, the formation of ammonium sulphate is favourable at high relative humidity and low temperatures (Stockwell et al. 2000).

A seasonal variation of 13.73 % was obtained in this study (calculated from the difference between the unit and the average summer/winter concentration ratio, and expressed as a percentage).

Other authors have reported on seasonal variations of ammonia. Behera and Sharma (2010) evaluated ammonia levels in Kampur (IIT Kampur and Colonelganj). They found average ammonia concentrations higher than in Madrid City, with seasonal variations of ammonia of 10.43% (IIT Kampur) and 8.71% (Colonelganj). Phan et al. (2013) assessed ammonia concentrations in Seoul from two administrative districts: Gwang Jin and Gang Seo from September 2010 to August 2011. They obtained a seasonal variation (summer/winter) of ammonia of 57.00% and 53.18% in Gwang Jin and Gang Seo, respectively.

Ammonia levels in Madrid City vs traffic density, garbage containers and sewage system were assessed in order to identify possible local emission sources that could contribute to public health risk. Ammonia concentrations and traffic density data are shown in Table 2. A linear regression was calculated where the independent variable was the traffic density and the dependent one was the ammonia concentration. Pearson's correlation coefficient ($r = 0.6859$) showed a significant relationship between both variables. The linear regression coefficient showed a predictive capability of the independent variable close to 50% ($p>0.05$, $N=14$). Due to the influence of the temperature on ammonia levels in ambient air, a relationship between ammonia concentrations and traffic density in winter and summer was conducted. The results showed significant relationships between the variables, with a higher correlation coefficient in winter. It is important to note that the sample sizes for these correlation analyses are small. However, it would seem likely that similar trends would apply with larger sample sizes.

The distances of garbage containers and sewers relative to the positions of the air samplers are presented in Table 3. Ammonia concentrations decreased 0.07 and 0.74 $\mu g/m^3$ per meter of distance from garbage containers and sewers to measurement point, respectively. High correlations ($r = 0.996$ and 0.883) were obtained between ammonia concentrations and distances from garbage containers ($N = 20$) and sewers ($N = 14$), respectively. Wolseley et al. (2006) found a decrease in the ammonia concentrations while increasing the distance from emission sources. Reche et al. (2012) evaluated the relationship between ammonia concentrations and the distance to garbage containers. They reported on a decrease from around 9 $\mu g/m^3$ to 4.5 $\mu g/m^3$ in less than 30 m.

Many authors studied the horizontal reduction of the ammonia levels with respect to other emission sources. Krupa (2003) reported on a reduction of 50% of the ammonia concentration at 600 m from a source. Wilson and Serre (2007) observed a decrease of 0.01 $\mu g/m^3$ per meter of distance from a source.

Based on above information, traffic load and other local emission sources for ammonia could be present in urban areas, and factors such as ventilation effect at the measurement point could play an important role about ammonia concentrations in urban environment (Tanner 2009).

A total of 40 clusters were estimated in order to establish a reliable air quality monitoring network for ammonia in Madrid City. Concentration value to each cluster was the average ammonia concentration estimated by IBM SPSS Statistic v22 and represented a sampling site. This point presented the lower standard deviation respect to the average ammonia concentration of the cluster. Based on that one, a minimum value of 0.08 $\mu g/m^3$ for the Euclidean distance and a maximum value of 0.06 $\mu g/m^3$ for the standard deviation were set for each cluster (Fig. 3). Information percentage obtained using the minimum clusters number ($N=40$) is similar to that obtained from all sampling points ($N=110$). Information percentage is defined as provided information using 40 or 110 sampling points, and was calculated using a lineal regression model between estimated concentration (ammonia concentrations calculated by clustering process, $N=40$) and analyzed concentration (ammonia concentrations evaluated in field, $N=110$), and therefore, represents the correlation between the information obtained by 40 and 110 sampling points, respectively. However, a significant number of clusters lower than 40 would leads to a variation in the spatial distribution of the ammonia concentration respect to the distribution obtained in the iso-concentration maps with 110 clusters in Madrid City. This fact would conducts a lack of information. For this reason, the final clusters number was set at 40 because these 40 samples would provide information as reliable as 110 samples and would provide essentially all of the information that was needed to assess the situation regarding ammonia concentrations in the air of Madrid City. This procedure provides a useful tool to evaluate the air quality from a minimum number of representative sampling points in urban environments by diffusive samplers.

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Table 1 Statistical summary of ammonia concentrations in Madrid City from November 19-26, 2014 (winter campaign) and July 1-8, 2015 (summer campaign) and meteorological data

Parameter	**$[NH_3]$, µg/m^3**	
	Winter campaign	**Summer campaign**
Maximun	11.23	11.08
Minimun	0.39	2.33
Mean	4.66	5.30
Standard deviation	2.14	1.81
Percentile 25	3.41	3.99
Percentile 50	4.48	5.16
Percentile 75	5.74	6.37
Mean temperature (ºC)	11.8	30.7
Relative humidity (%)	81.5	24.6
Precipitation (mm)	4.2	0.0
Speed wind (km/h)	5.8	11.9

Table 2 Traffic density and ammonia concentrations

Sample code	**Traffic station**	**Traffic density (vehicles/day)**		**$[NH_3]$, µg/m^3**	
M188	Station 13	Winter	380,949	Winter	6.05
		Summer	406,345	Summer	4.57
M240	Station 15	Winter	214,001	Winter	6.70
		Summer	203,368	Summer	7.33
M278	Station 27	Winter	443,352	Winter	10.52
		Summer	460,689	Summer	11.08
M226	Station 28	Winter	223,242	Winter	4.23
		Summer	259,048	Summer	4.43

M205	Station 32	Winter	203,422	Winter	6.67
		Summer	194,401	Summer	7.26
M189	Station 49	Winter	165,427	Winter	2.52
		Summer	164,868	Summer	4.34
M176	Station 58	Winter	103,311	Winter	3.68
		Summer	94,383	Summer	3.03

Table 3 Distance of diffusive samplers from garbage containers and sewers

	Distance (m)	**Number of samplers**		**Distance (m)**	**Number of samplers**
Garbage containers	1.5	10	**Sewers**	0.5	3
				1.5	4
	6.0	6		2.5	2
				3.5	2
	20.0	4		4.5	2
				6.0	1

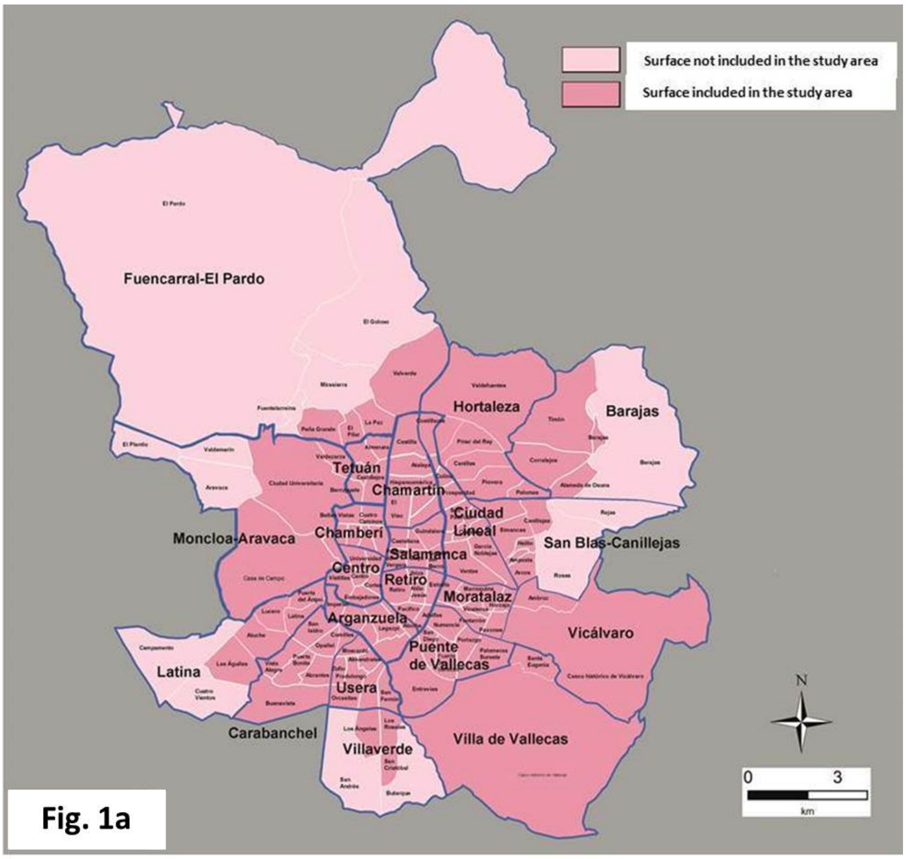
Surface not included in the study area
Surface included in the study area
Fuencarral-El Pardo
Hortaleza
Barajas
Tetuán
Chamartín
Ciudad Lineal
Moncloa-Aravaca
Chamberí
Salamanca
San Blas-Canillejas
Centro
Retiro
Moratalaz
Arganzuela
Vicálvaro
Puente de Vallecas
Latina
Usera
Carabanchel
Villaverde
Villa de Vallecas
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Fig. 1a

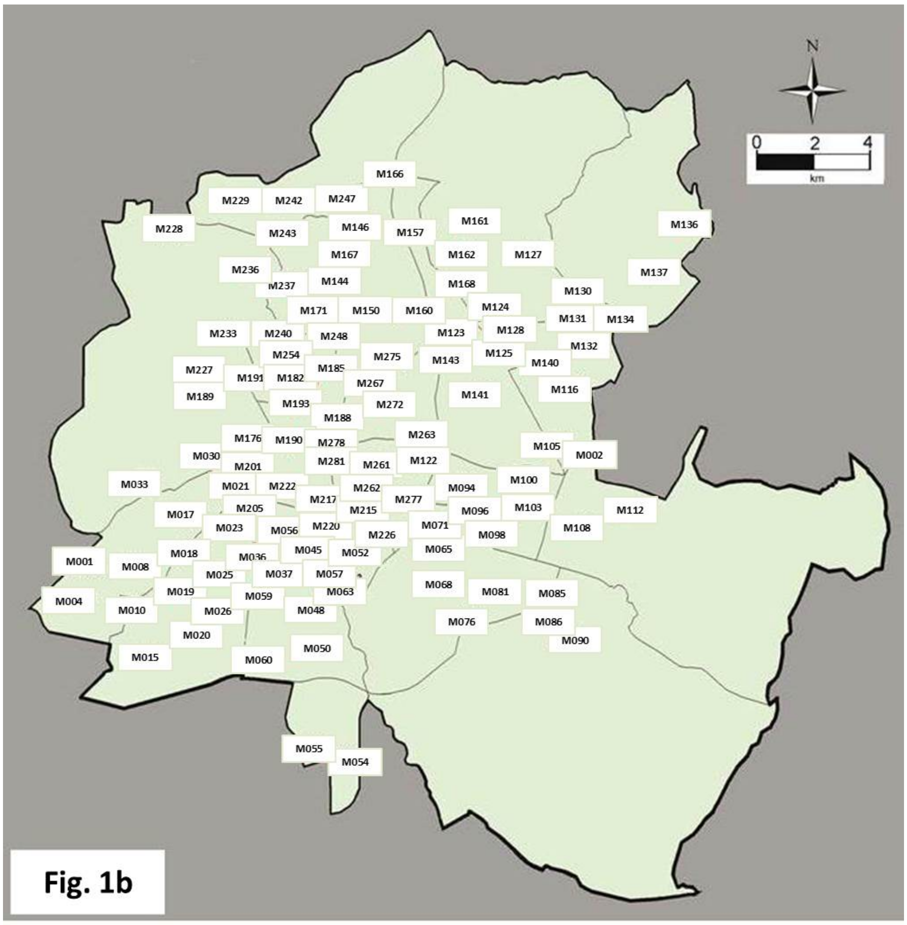

Fig. 1b

Fig. 1 (a) Surface of Madrid City (districts and neighborhoods); **(b)** Locations of sampling points in Madrid City

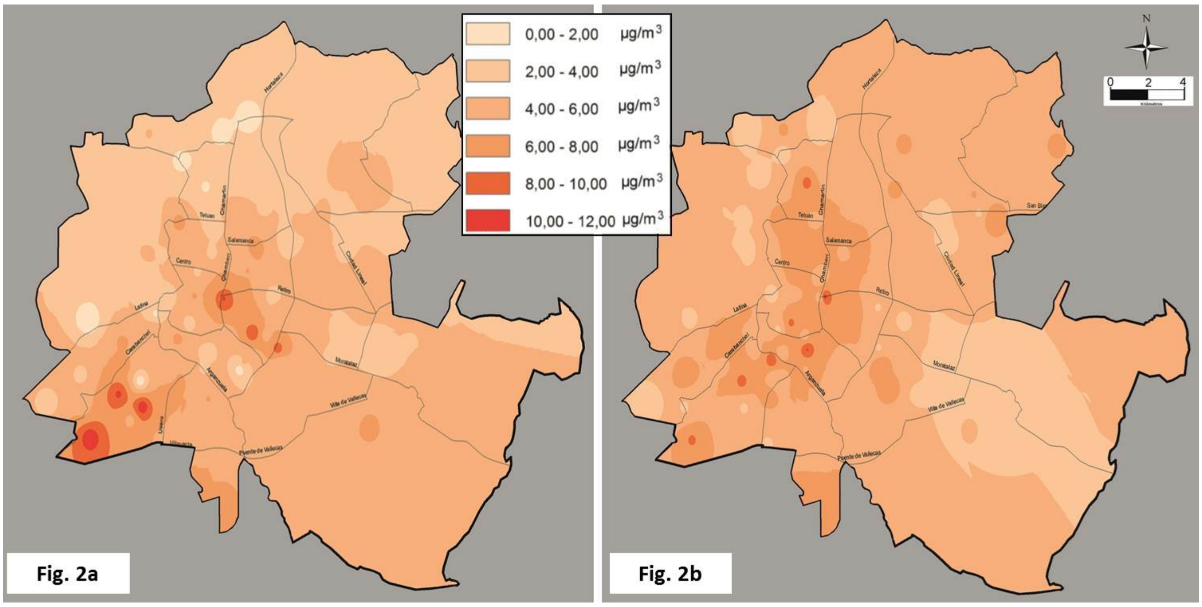

Fig. 2a

Fig. 2b

Fig. 2 Iso-concentration maps of ammonia in Madrid City. **2a** Winter campaign. **2b** Summer campaign

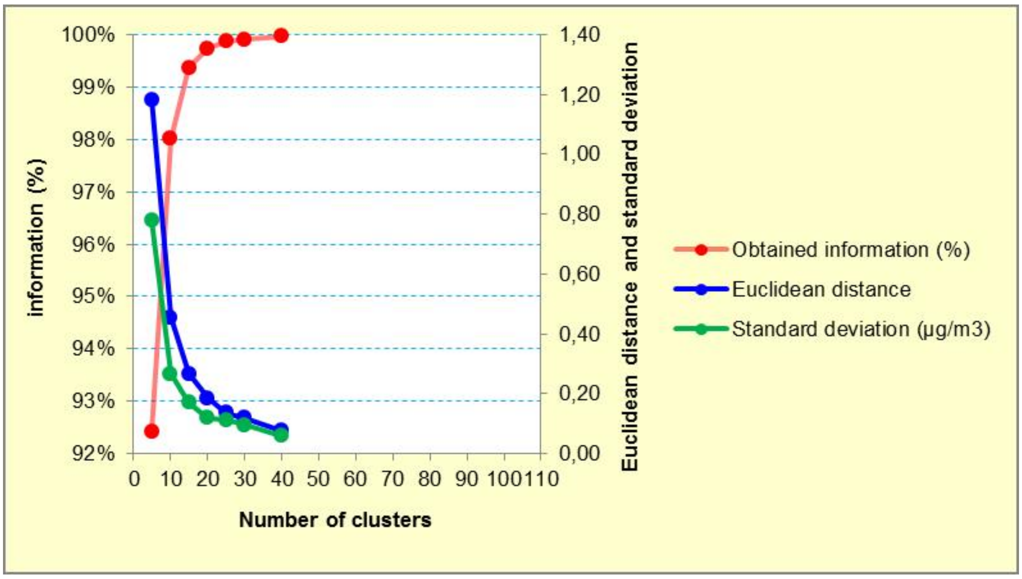

Fig. 3 Number of clusters as a function of Euclidean distance, standard deviation and obtained information percentage