Deposição atmosférica de poeira e níveis de elementos traço numa cidade industrial com clima Mediterrânico

Atmospheric dust deposition and levels of trace elements in an industrial city with a Mediterranean climate

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Resumo: Este estudo foi realizado para examinar a influência de um complexo industrial, e o elevado volume de tráfego associado, na deposição de poeira atmosférica numa cidade com clima mediterrâneo. O dispositivo comumente utilizado para recolher a deposição atmosférica total consiste num sistema composto por um funil ligado a uma garrafa coletora. Dois sistemas foram colocados nas áreas exteriores de duas escolas (Escola Básica Visconde de Salreu e Escola Secundária de Estarreja) localizadas poucos quilómetros a sul do complexo industrial de Estarreja. A recolha de amostras foi realizada mensalmente de maio de 2018 a setembro de 2018. Nas amostras solúveis não tratadas foi determinada a condutividade elétrica bem como a concentração de alguns aniões por cromatografia iónica. O teor de elementos traço nas frações solúvel e insolúvel da deposição atmosférica de poeiras foi determinado por ICP-MS. Os resultados sugerem padrões de variação temporal semelhantes para o fluxo de deposição de cobre e zinco solúvel, e um padrão de variação distinto para fluxo de deposição do zinco insolúvel.

Palavras-chave: poeira atmosférica, deposição atmosférica, elementos potencialmente tóxicos, fracção solúvel, fracção insolúvel

Abstract: This study was performed to examine the influence of an industrial complex, and the high traffic volume associated with it, on the atmospheric dust deposition in a Mediterranean setting. The most frequently used device for collecting total atmospheric wet and dry deposition consists of a funnel connected to a receiving bottle. Two deposition collectors were placed in exterior areas of two schools (Escola Básica Visconde de Salreu and Escola Secundária de Estarreja) located a few km south from the industrial complex of Estarreja. Sample collection was performed from May 2018 to September 2018 on a monthly basis. Soluble untreated samples were analysed for electrical conductivity and anions by ion chromatography.The pseudo-total trace elements content in soluble and insoluble fractions of atmospheric dust deposition were determined by inductively coupled plasma - mass spectrometry (ICP-MS). The results obtained suggest similar temporal variation patterns for the deposition flux of soluble copper and zinc and a distinct variation pattern for the atmospheric deposition of insoluble zinc.

Keywords: airborne dust, atmospheric deposition, potentially toxic elements, soluble fraction, insoluble fraction

1. Introduction

Metal(loid) transfer through the atmosphere is a significant part of the biogeochemical cycle of these elements. There are different host sources of components that strongly affect the composition of airborne dust in the Mediterranean area. There are natural (marine, terrigenous, biological) and anthropogenic sources (industrial, traffic, burning of fossil fuels and biomass, agricultural and mining activities). However, the levels and host sources are difficult to distinguish (Bisquert et al. 2017).Atmospheric elemental pollutants are transported over long distances in very small particles. These particles when aggregated or washed out by rain are called atmospheric deposition, both dry and wet. Dry particle deposition occurs by direct impact or by gravitational settling on land or water surfaces. In wet deposition, ions, aerosols and gases are dissolved or suspended in water droplets or ice crystals. Besides such long-range transportation processes, considerable dry and wet depositions also occur locally. Since metal(loid)s usually present high toxicity and high lability in atmospheric particulate matter, their monitoring is important. This study was performed to examine the influence of an industrial complex, and the high traffic volume associated with it, on the atmospheric dust deposition in a Mediterranean setting.

2. Methods

2.1. The study area

Estarreja is a coastal municipality located in the centre of Portugal that extends over an area of 108.2 km^2 and has an estimated resident population of 26997 inhabitants (CCDR 2011).The climate is Mediterranean temperate (type Csb according to the Koppen–Geiger climate classification system), characterised by dry and warm summers, with an average annual temperature of 15.5ºC and an average annual relative humidity of 78%. In 2018, the wind has blown predominantly from NW, with an average velocity of 0.2 to 0.4 m s^{-1}. The geology is characterised by the predominance of Quaternary sands and clays deposited in dune, beach and lagoon environments. The municipality encompasses one of the most important industrial complexes of the country, known as the chemical complex of Estarreja (CCE). Since the 1950s, the complex has produced a variety of organic and inorganic compounds, such as fertilizers from sulphide ores, nitric acid, aniline, nitrobenzene, chlorate compounds from rock salt, polyurethanes and others (Marinho Reis et al. 2018). Data available for the study area from the QualAr database, the Portuguese online database for air quality monitoring, show that during sample collection, only NOx, levels (daily average) were occasionally above the 25 µg m^{-3} limit value established by the European Commission (EC) 2008/50 Framework Directive for air quality parameters and pollutants. Other monitored air pollutants such as sulphur dioxide (SO_2) and nitrogen dioxide (NO_2), ozone (O_3), PM_{10} and $PM_{2.5}$ were below the legislated limits.

2.2. Sampling

The most frequently used device for collecting total atmospheric wet and dry deposition consists of a funnel connected to a receiving bottle. When aerosol deposition settles on the funnel wall, they adhere easily and accumulate on its walls and are then transferred to the bottle during a rain event or by rinsing the funnel at the end of each collection period (Azimi et al., 2003).Two deposition collectors (a and b, Fig. 1) were placed in exterior areas of two schools (Escola Básica Visconde de Salreu and Escola Secundária de Estarreja) located a few km south from the industrial complex of Estarreja. The two sites were selected specifically to assess the impact of anthropogenic activities on this urban area. Sample collection was performed from May 2018 to September 2018 on a monthly basis.

2.3. Samples processing and analysis

After one month in place, the sampling systems were replaced with new ones and later transported to the laboratory for processing. Soluble untreated samples were analysed for electrical conductivity (dS/m) and anions (Cl^-, NO_3^-, SO_4^{2-}) by ion chromatography. The pseudo-total trace elements content in the insoluble fraction was determined through an acid digestion in

a hot plate. One blank sample was prepared using the same agents and quantities in each batch. In the case of the soluble fraction, trace elements assessment was made directly from the acidified aliquot. Concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Ga, Mn, Ni, Pb, Sb, Sn, Ti, V, Zn, and Zr were determined by inductively coupled plasma - mass spectrometry (Perkin Elmer Nexlon 300 X). The data used in this study report to the average values obtained from the two bottles used in the sampling system.

Fig. 1 – Sampling system composed of a funnel connected to a bottle (systems a and b), used to collect total atmospheric wet and dry deposition.

3. Results and discussion

3.1. Total dust deposition

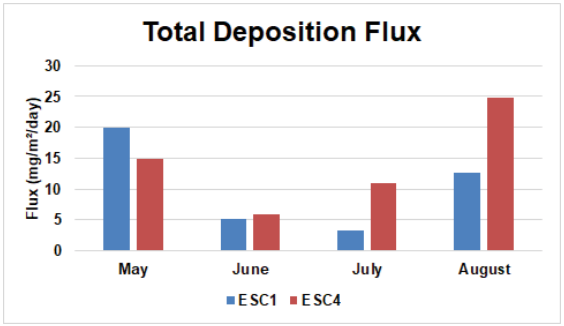

Fig. 2 – Variation in total dust deposition in the study area from May to August of 2018.

The flux of particle deposition registered in the study area ranged from 3.33 to 24.87 mg m^{-2} day^{-1}. The sampling station that registered greater deposition flux from May to August 2018 was Escola Básica Visconde de Salreu, in August (24.84 mg m^{-2} day^{-1}). The lowest deposition flux occurred in Escola Secundária de Estarreja, in July. During the monitoring period, both schools showed a similar trend, with a marked decrease in the deposition flux during the months of June and July (Fig. 2).

3.2. Trace elements deposition

Table 1 shows summary statistics for concentrations of total atmospheric deposition for the elements under study.

Tab. 1 – Descriptive statistics for total atmospheric deposition of the chemical elements under study, expressed as µg m^{-2} day^{-1}.

	mimum	median	maximum	mean	std
Al	43.616	87.277	483.397	127.210	147.234
As	0.085	0.210	0.392	0.218	0.117
Cd	0.002	0.006	0.016	0.007	0.005
Co	0.018	0.063	0.165	0.071	0.051
Cr	0.167	0.263	0.765	0.357	0.219
Cu	2.577	7.233	17.141	8.379	5.317
Fe	9.878	69.105	389.047	100.087	121.063
Ga	0.007	0.022	0.148	0.039	0.045
Mn	1.334	2.265	7.096	3.271	2.223
Mo	0.029	0.063	0.084	0.056	0.021
Ni	0.895	2.314	7.069	2.986	2.213
Pb	0.208	0.420	0.859	0.442	0.206
Sb	0.046	0.093	0.195	0.101	0.056
Sn	0.039	0.091	0.493	0.148	0.148
Ti	0.207	1.842	6.114	2.236	1.970
V	0.117	0.208	0.765	0.289	0.207
Zn	5.858	13.214	40.195	17.039	12.074

From the major elements, Al shows the higher and Ti the lower concentration of atmospheric deposition. For trace elements, Zn and Cu are the potentially toxic elements (PTEs) with more elevated deposition fluxes. Elements that were found mainly in insoluble phases include Al, Fe, Ga, Pb, Sn, and Ti. Trace elements such as As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Sb, V, and Zn, are in the dust mainly associated with soluble phases. Given that Zn and Cu have elevated deposition fluxes, and that the most important contribution comes from soluble phases, it was decided to study these two PTEs with further detail.The flux of particle deposition is higher for Zn (0.99 - 34.48 µg m^{-2} day^{-1}) than for Cu (0.03 – 11.98 µg m^{-2} day^{-1}), both in insoluble and soluble phases. These PTEs are mainly associated with the soluble phase, except in May for Zn and August for Cu. This variation is similar in both study areas, suggesting some mobility for these trace elements.

The soluble fraction deposition variation pattern during the monitoring period is similar for the two PTEs, showing a marked decrease in June followed by a slight increase in the months of July and August. A

distinct result was obtained for the insoluble fraction of the two elements. Insoluble Cu shows a higher deposition flux in May, which is in agreement with a higher deposition flux of soluble Cu (Fig. 3) and an elevated total dust deposition flux in both schools (Fig. 2). This result suggests that the event associated with a more elevated total dust deposition in May was characterised by elevated Zn and Cu deposition, in both soluble and insoluble forms. However, the event associated with a more elevated total dust deposition in August, especially in Esc 4 (Escola Básica Visconde de Salreu), was characterised by an elevated deposition flux of insoluble Zn (Fig. 4) and soluble Cu (Fig.3).

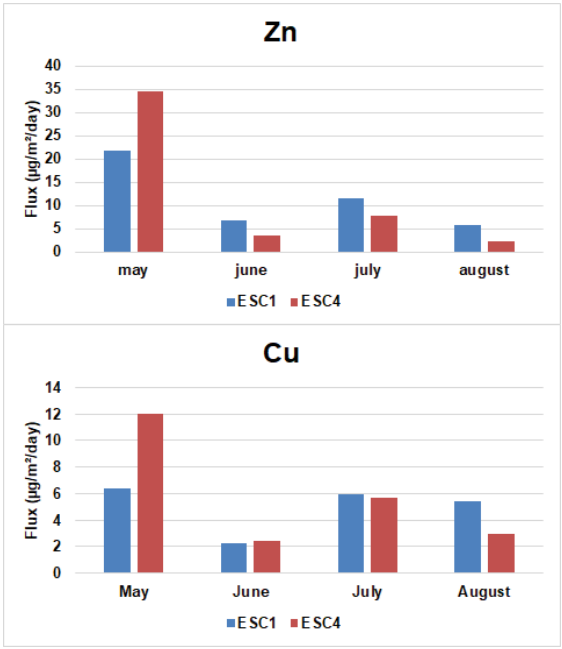

Fig. 3 – Variation is soluble Zn and Cu deposition in the study area from May to August 2018.

4. Conclusions

The results suggest that total dust deposition in May was more influenced by atmospheric aerosols while in August it seems associated mostly with atmospheric dust.

Acknowledgments

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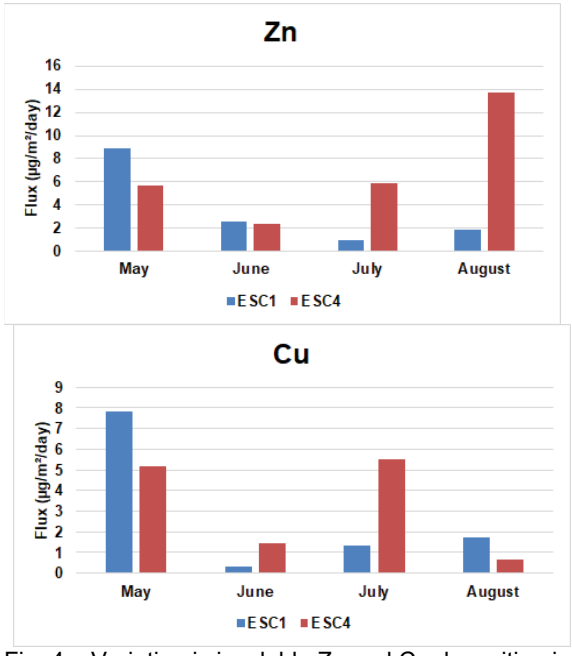

Fig. 4 – Variation is insoluble Zn and Cu deposition in the study area from May to August 2018.

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