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Composition and source apportionment of fine particulate matter during extended calm periods in the city of Rijeka, Croatia

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ABSTRACT

In the city of Rijeka, Croatia, an extended, two-year aerosol pollution monitoring campaign was recently completed. During that period, 345 samples of fine fraction of aerosols were collected on stretched Teflon filters. All samples were analyzed by Ion Beam Analysis techniques Proton Induced X-ray Emission and Proton Induced γ-Ray Emission and concentrations of 22 elements were determined. Concentrations of black carbon were determined by Laser Integrated Plate Method.

For the Bay of Kvarner, where the city of Rijeka is located, long periods of calm weather are common. As a consequence, during these periods, air pollution is steadily increasing. To pin-point and characterize local, mostly anthropogenic, air pollution sources, only samples collected during the extended calm periods were used in this work. As a cut-off wind speed, speed of 1.5 m/s was used. In that way, out of all 345 samples, only 188 were selected. Those samples were statistically evaluated by means of positive matrix factorization. Results show that from all anthropogenic sources (vehicles, secondary sulphates, smoke, heavy oil combustion, road dust, industry Fe and port activities) only secondary sulphates and heavy oil combustion were significantly higher (40% and 50%, respectively) during calm periods. On the other hand, natural components of aerosol pollution such as soil and sea salts, (typically present in concentrations of 1.4% and 9%, respectively) are practically non-existent for calm weather conditions.

1. Introduction

During the past few decades, atmospheric particulate pollution has been a subject of intense research due to it's strong negative impact on the human health [1,2]. Concentrations and composition of fine particulate matter ($PM_{2.5}$), was therefore a major public concern, especially for urban areas.

To assess fine aerosol pollution in the city of Rijeka (latitude 45°21′N, longitude 14°26′E), Croatia, long term sampling campaign was initiated in 2013. Rijeka is the biggest Croatian port and third Croatian city by size with approximately 130 000 inhabitants. Sampling site was located in the Port of Rijeka and close to the city center so it was in a close proximity of several strong pollution sources: harbour (cargo traffic of about 10 Mt/year), road and rail transport, shipyard (the biggest in Croatia), oil refinery, oil powered thermal plant (320 MW; closed down in 2015), and coal powered thermal plant Plomin (Fig. 1).

As it can be seen from the Fig. 1, city of Rijeka is situated at NE coast of the Bay of Kvarner. Rijeka is open to the sea from the south side and surrounded by the mountains on east, north and west side. Such a terrain contributes to the accumulation of fine aerosol pollution during long periods of calm weather. As a consequence, during these periods, air pollution is steadily increasing. Similar episodes of increased pollution during calm weather are already reported by a number of researchers. Following are few examples: a) Auckland (New Zealand); during calm weather, higher concentrations of vehicle emission and sulphate were obtained [3]; b) Venice (Italy); due to low wind speed (<1.6 m/s) in semi- rural area near Venice higher average concentrations of combustion, road traffic, secondary sulphate and secondary nitrate were measured [4].

Sampling campaign started on August 6, 2013 and ended on October 1, 2015. During that period 345 daily samples were collected. To pin-point and characterize local air pollution sources, used were only daily samples collected during relatively calm periods when average wind speed was less than 1.5 m/s. In this way, only 188 samples were selected and used in this work. Every

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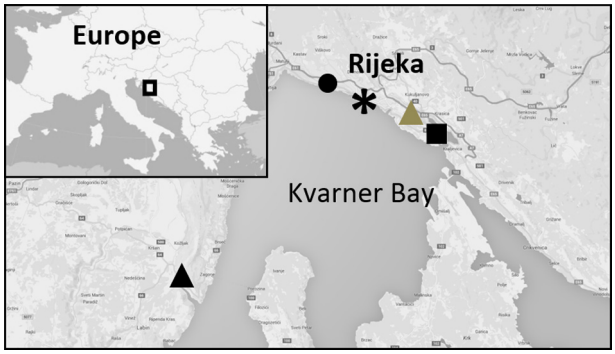

Fig. 1. Sampling site of $PM_{2.5}$ in Rijeka (Croatia) – star; black point – shipyard "3 Maj", grey triangle – TPP oil (oil powered thermal plant), black triangle TPP coal – (coal powered thermal plant), black square – Oil refinery.

sample was analyzed by Particle Induced X-ray Emission (PIXE) and Proton Induced Gamma-ray Emission (PIGE) to obtain concentrations of 22 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr and Pb. Laser Integrated Plate Method (LIPM) was used to determine concentrations of black carbon (BC).

2. Experimental

2.1. Sample collection

Sampling site was located in the Port of Rijeka, close to the main bus stop and two busy roads with an average traffic intensity of 25–30 thousand cars, trucks and buses per day.

$PM_{2.5}$ samples were collected 4 times a week during the 18 months period.. The sampler inlet was positioned 3 m above the sea level, 2 m above the ground level and 30 m away from the main road. All samples were collected during 24 h periods.

Cyclone sampler based on ANSTO ASP sampler [5] was used to collect $PM_{2.5}$ aerosols on a stretched Teflon filters (PALL Corporation R2P1025, diameter of 25 mm, 3 μm pore size) with the average flow rate of (22.5 ± 3) l/min.

2.2. Analysis

Each Teflon filter was weighted before and after exposure at the Institute for Environmental Research, Australian Nuclear Science and Technology Organisation (ANSTO). The total $PM_{2.5}$ mass was obtained by Mettler Toledo MX5 microbalance under the conditions of 22 °C and relative humidity of 50%, with uncertainty ± 10 μg, readability 1 μg, repeatability 0.8 μg.

All aerosol samples were analyzed by PIXE technique in one of the two laboratories: Laboratory for Ion Beam Interactions, Ruđer Bošković Institute (RBI), Zagreb and Institute for Environmental Research (ANSTO), Australia. For this study, majority of the samples were analyzed at RBI, exactly 155 samples, and at the ANSTO laboratory only 33 samples. At the RBI measurements were performed using 3 nA beam of 1.6 MeV and total collected charge was 3 μC. At ANSTO, PIXE and PIGE techniques were applied using 12 nA beam of 2.6 MeV protons and collection charge of 3 μC. GUPIX software [6] was used for quantitative analysis ofthe PIXE spectra and detector efficiency and H value were determined using thin Micromatter standards (Al, SiO, KCl, CaF_2, ScF_3, Ti, V, Cr, Mn, Fe, Ni, Cu, ZnTe, GaP, Ge, SrF_2 and MoO_3) were used for calibration of both X-ray detectors used with nominal area densities between 15 and 50 μg/cm^2 and uncertainties of ±5%. By using PIXE, concentrations of elements from Na to Pb were determined. uncertainties for major elements were from 6% to 8% (S, K, Ca, Fe, Zn) and minor elements were higher than 7% (Al, Si, P, Cl, Ti, V, Cr, Mn, Co, Ni, Cu, Br, Sr, Pb). Uncertainties in concentrations of Na (PIGE-ANSTO and PIXE-RBI) ranged from 6% to 18%. Minimum detection limits (MDL) by PIXE technique at RBI ranged from 0.2 ng/m^3 (Br) to 4.4 ng/m^3 (S), by PIXE at ANSTO ranged from 0.48 ng/m^3 (Zn) to 4.2 ng/m^3 (Al) and by PIGE at ANSTO was 62 ng/m^3 (Na). In our previous work [7] we presented comparison among the concentrations obtained in both laboratories. To summarise, concentrations of elements above corresponding MDLs, obtained by both laboratories were in agreement within approximately ±2%. More details of both analytical procedures and experimental setup (PIXE at RBI and, PIXE and PIGE at ANSTO) and analytical procedures used are reported in our papers [7,8].

To obtain black carbon concentrations (BC), Laser Integrating Plate Method (LIPM) was used at the Laboratory for elemental microanalysis (LEMA) in Rijeka, assuming a mass absorption coefficient of 7.02 m^2/g. Uncertainties in concentrations of BC ranged from 7% to 10% and average MDL was 28 ng/m^3 [7,9].

3. Results and discussion

In Table 1, average annual concentrations of fine particulate mass are presented for entire sampling period (all days) and days with calm weather conditions It should be pointed out that for the fine particulate mass the EU Directive 2008/50/EC [10] is defining only annual limit value of 25 μg/m^3 (no daily limits are given). From the Table 1 can be seen that the calculated annual average of measured $PM_{2.5}$ fraction did not exceed prescribed limit value for all weather condition for all three years. However, for days with calm weather condition, calculated annual average slightly exceeds prescribed limit value for 2013 and 2015. This is an expected consequence of the pollution accumulation effect, which happens during calm periods.

To get more detailed relation between $PM_{2.5}$ concentration and wind speed, the mean concentrations of all measured samples (345 days) was correlated with the average wind speed for the corresponding day. Results are shown in Fig. 2. Mean concentrations of $PM_{2.5}$ are clearly decreasing with increasing wind speed. However, for seven days with wind speed higher than 4.6 m/s, mean concentrations of $PM_{2.5}$ were higher. This is probably due to higher contribution of the natural components such as soil dust and sea spray and/or long distance transport from central Europe. However, due to relatively low statistics, no conclusive answer has been derived at this point. This phenomenon will therefore be subject of our future research.

Significant seasonal variation of $PM_{2.5}$ concentrations is shown in Fig. 3. From this figure, it is obvious that winter concentrations are 2 to 3 times higher than summer concentrations. By analysing individual elements/components of $PM_{2.5}$ it was found that mostly potassium and black carbon have higher concentrations during winter season. Potassium is coming mostly from the wood burning processes used for domestic heating. During winter periods this source is typically contributing with 20% of the total $PM_{2.5}$ mass. As it can be seen from the Fig. 3, if only samples collected during calm days were included (Fig. 3, black dots) the contribution is even higher.

Black carbon is coming from several sources such as road traffic (up to 40%), wood burning (up to 20%) and local industry (heavy oil combustion, BC had contribution up to 10%) [7].

3.1. PMF source profiles and contributions

To unfold key source fingerprints and their contribution to the total $PM_{2.5}$ pollution positive matrix factorization (PMF) was performed. The original Paatero DOS version of the PMF codes (PMF2) was used [11,12]. The results of the PMF analysis are

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