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Characterization and source apportionment of fine particulate sources at Rijeka, Croatia from 2013 to 2015

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ABSTRACT

$PM_{2.5}$ daily aerosol samples were collected in Rijeka, Croatia during period from 6th August 2013 to 29th January 2015. In total, 259 samples were collected on Teflon filters and analyzed by PIXE and PIGE techniques to give information on 21 elements from Na to Pb. Additionally, black carbon was determined with the Laser Integrated Plate Method.

Results were statistically evaluated using Positive Matrix Factorization (PMF). Eight major pollution sources: auto, smoke, secondary sulfates, heavy oil combustion, sea spray, road dust, industry iron and soil dust were identified together with their relative contributions in total $PM_{2.5}$ pollution.

1. Introduction

High concentrations of fine particles in the urban atmosphere have adverse impact on air quality and consequently on human health [1–3]. The identification and characterization of emission sources and their contribution to the ambient concentration of pollutants has been one of the major focus in urban air quality research.

The city of Rijeka (latitude 45°21′N, longitude 14°26′E) is the largest Croatian port, and the third city by size in the Republic of Croatia with approximately 130,000 inhabitants. The industrial complex, oil powered thermal plant 320 MW (TPP) and oil refinery (OR), are located 9 km eastward from the city center. Other possible pollution sources in this region are coal powered thermal plant of 330 MW located at the Port Plomin (30 km southwest from Rijeka) and industrial complex located in Trieste (60 km northwest from Rijeka) with a very busy port, oil refinery and an 400 MW oil power plant (Fig. 1).

Average daily wind speed was relatively low, averaging at the 1.6 m/s [4], which often caused accumulation of air pollution in the bay of Rijeka.

During the 1.5 years sampling period (from August 2013 to January 2015) 259 daily $PM_{2.5}$ samples were collected. Samples were analyzed with Laser Integrated Plate Method (LIPM), Proton Induced X-ray Emission (PIXE) and Proton Induced Gamma-ray Emission (PIGE). The results obtained by LIPM, PIXE and PIGE techniques were statistically evaluated using Positive Matrix Factorization (PMF) with the intention to identify major sources contributing to the fine particle emission.

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 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 (6th August 2013 to 29th January 2015). Due to the technical problems with the sampler, samples were not collected in the period from 5th May to 5th August 2014. 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. In total, 259 samples were collected.

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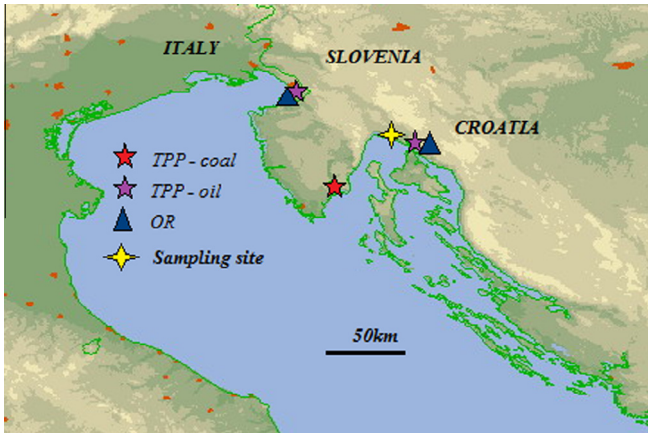

Fig. 1. Location of sampling site in Rijeka, thermal powered plants (TPP–oil and TPP–coal) and oil refinery (OR).

2.2. Analysis

The total $PM_{2.5}$ mass (Table 1) was obtained by gravimetric measurements with Mettler Toledo MX5 microbalance under the laboratory conditions of 22 °C and relative humidity of 50%, with uncertainty ±10 μg, readability 1 μ, repeatability 0.0008 mg at ANSTO.

All aerosol samples were analyzed by PIXE technique at two laboratories: Laboratory for Ion Beam Interactions, Ruđer Bošković Institute (RBI), Zagreb and Institute for Environmental Research (ANSTO), Australia. Majority of samples (202) were analyzed at RBI and only 57 samples at the ANSTO laboratory.

At the RBI measurements were performed using 3 nA beam of 1.6 MeV protons. Beam diameter at the target was 5 mm and total collected charge was 3 μC. To measure wide range of elements, two X-ray detectors were used: SDD (Ketek Vitus H20, 8 μm Be window and 450 μm Si crystal thickness) placed at 150° for detection of low energy characteristic X-rays (from Na to Fe) and a Si(Li) detector (Canberra, model SSL80155) placed at 145° for detection of more energetic X-rays [6]. To optimize it for detection of higher energy characteristic X-rays (>3 keV) a 360 μm thick Mylar film was put in front of it to completely attenuate X-rays below 3.0 keV. Both detectors were carefully calibrated using set of single element Micromatter thin standards evaporated on thin Nucleopore (polycarbonate) filters. One multielemental standard (Vienna Dust Standard V98, Air particulate matter on filter media) was also measured. GUPIX software [7] was used for quantitative analysis of the PIXE spectra and results were compared with the certified values.

At ANSTO, PIXE and PIGE techniques were used simultaneously using 12 nA beam of 2.6 MeV protons with 8 mm diameter and collection charge of 3 μC. Characteristic X-rays were measured with SDD (165-VTX-EM) positioned at 145° for detection characteristic X-rays. Measurements of absolute elemental concentrations in thin samples were obtained through normalization to known thin Micromatter reference material with typical areal density of approximately 50 $\mu g/cm^2$ and quoted accuracy of ±5% [8]. The following six foils were used to cover the X-ray region from 1 keV to 20 keV: Al, Si, NaCl, CaF_2 and SrF_2. For calibration of PIGE detector (Ge detector Canberra GC3020) Na and F reference foils were used. The following elements were measured by PIXE: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb while PIGE was used to measure only sodium.

Typical uncertainties in measurements of concentrations by PIXE (ANSTO and RBI) for major elements were from 6% to 8% (S, K, Ca, Fe, Zn) and for minor elements were from 7% to 100% (Al, Si, P, Cl, Ti, V, Cr, Mn, Co, Ni, Cu, Br, Sr, Pb) [6,8]. Uncertainties in concentrations of Na (PIGE and PIXE RBI) ranged from 6% to 18%.

To obtain black carbon (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 [9]. Uncertainties in concentrations of BC ranged from 7% to 10%.

Table 1
Average concentrations, standard deviations (SD), medians, maxima, minimum detection limits (MDLs) in ng/m^3 and the number *N* of samples above MDL (*N*) for 259 samples collected in Rijeka from period 6th August 2013 to 29th January 2015 obtained by PIXE, PIGE and LIPM.

El	Avg	SD	Med	Max	MDL–RBI (ANSTO)	*N*
Na	117	113	80.6	757	2.8 (62)	257
Mg*	22	33	12	329	2.2	200
Al	44	77	22	650	2.2 (4.2)	255
Si	110	196	54	1811	2.2	259
P	2.8	6.9	1.2	93	3.6 (2.1)	103
S	789	526	668	2975	4.4 (1.9)	259
Cl	54	156	8	1445	2.5	228
K	194	278	116	2983	3.0 (1.2)	259
Ca	88	90	56	681	1.8	258
Ti	3.4	4.7	1.9	34	2.5	253
V	3.4	4.7	2.5	48	0.4 (0.84)	231
Cr	0.6	0.5	0.5	5.8	0.42 (0.78)	158
Mn	4.4	10	2.4	153	0.32 (0.62)	259
Fe	93	73	74	493	0.24 (0.56)	259
Co	0.49	0.65	0.33	7.5	0.28 (0.59)	12
Ni	1.9	1.8	1.5	18	1.4 (1.8)	244
Cu	4.4	11	2.6	150	0.23 (0.63)	259
Zn	14	11	11	67	0.25 (0.48)	259
Br	2.6	1.9	2.2	19	0.2 (0.57)	218
Sr	1.5	5.7	0.39	75	0.96	45
Pb	6.8	25	4.0	404	2.3 (3.7)	217
BC	3439	1334	3357	8750	28	259
$PM_{2.5}$	20,600	8050	20,200	51,500		

* 202 samples.

3. Results and discussion

Results of PIXE and PIGE (ANSTO and RBI) are found to be in very good agreement especially for elements with concentrations above corresponding MDLs.

In Fig. 2 presented is comparison between concentrations of Na and Zn obtained by the two laboratories, ANSTO and RBI. Concentrations of Na obtained by PIXE at RBI were approximately 1% higher than corresponding concentrations obtained by PIGE at ANSTO. Similarly, concentrations of Zn obtained at RBI were approximately 1% lower than corresponding concentrations obtained at ANSTO. In general, concentrations obtained at these two laboratories differed for approximately ±2%.

In Table 1, average concentrations of all measured elements, their standard deviations, medians, maxima and minimum detection limits (MDL) are given for all samples. In the last row we presented daily average, median and maximum of fine mass. It should be noted that for the fine mass the EU Directive 2008/50/EC [10] is defining only annual limit value of 25 $\mu g/m^3$ (no daily limits are given). As it can be seen from the Table 1, BC is dominant component with the mean concentration of 3439 ng/m^3, followed by S, K, Na, Si, Fe, Ca and Cl which are indicating both anthropogenic and natural sources of $PM_{2.5}$. To unfold key source fingerprints and their contribution to total $PM_{2.5}$ pollution PMF statistical method was used as discussed below.

3.1. PMF source profiles and contributions

We applied Positive Matrix Factorization (PMF) to identify sources of fine particulates [11]. The original Paatero DOS version of the PMF codes (PMF2) was used [12]. The results of the PMF