ISSN 0554-6397
PRETHODNO PRIOPĆENJE
(*Preliminary communication*)

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Fine Particulate Matter from Ship Emissions in the Port of Rijeka, Croatia

Abstract

The impact of ship emissions on air pollution in harbours is probably one of the lesser-understood aspects of anthropogenic pollution. Vessels are often powered by relatively old engines and at the same time quality of fuels is often questionable. These factors have potential to significant increase air pollution in busy harbours. It is well know that V/Ni ratio higher than 2.5 are good indicators of heavy oil combustion from the ship engines. To evaluate this contribution to the air pollution in the harbour of Rijeka we measured concentrations of V and Ni in fine aerosols ($PM_{2.5}$).
Over the 300 fine aerosol samples were collected during the three years period (February 2012 – June 2015) and analyzed by two analytical techniques; X-ray Fluorescence and Laser Integrated Plate Method at the Laboratory for Elemental-Micro Analysis (Department of Physics University of Rijeka). Concentrations of 18 elements (Si to Pb) were obtained as well as the black carbon (BC) component. The results were statistically evaluated by means of the positive matrix factorization.
In nearly 15% of samples, concentration ratio (V/Ni) was found to be around 3 indicating that during those days the source that we named "ship emission" was present in fine aerosol pollution with major components such as S, BC and traces K, V, Fe, Cl, Br, Pb and Ni. This anthropogenic source represented approximately 10% from the total fine aerosol mass.

Keywords: $PM_{2.5}$, ship emissions, vanadium, nickel, V/Ni ratio

1. Introduction

Harbours are important for economic and social development of coastal areas but they also represent sources of anthropogenic emissions often located near urban centres and industrial areas. The main pollutants emitted by ship traffic are nitrogen oxides, sulphur oxides and particulate matter (PM) [1]. Ultrafine particle $PM_{0.1}$ emitted from diesel vessels have a higher negative effect to health than coarse particle ($PM_{2.5-10}$). The number of these particles per mass unit is several orders of magnitude larger than coarse particles. The ships emission can be seen as causing health problems to people living and working in coastal area. International shipping has been linked with increased

mortality in coastal regions, caused by cardiopulmonary and lung cancer attributed to emissions from ship exhaust [1, 2, 3]. Particles emitted from ship exhaust are shown to contribute significantly to marine cloud formation [1, 4].

However, the direct identification of ship emissions by means of specific tracers is complex. They are also markers for other types of combustion processes such as energy generation, petroleum refinery and other types of industrial processes, which are located on land in the vicinity of harbour areas. Numerous studies have succeeded in identifying specific tracers of shipping emissions. As tracers of combustion processes based on heavy fuel oil as the main fuel, vanadium (V) and nickel (Ni) are generally identify as markers of shipping emission. It is important that a characteristic value of V/Ni ratio between 2.5 to 4 is considered typical for ship emission [1, 5, 6, 7, 8, 9]. The increase of the V/Ni ratio in the harbour direction was essentially due to a decrease of Ni concentrations, rather than to an increase of V concentration. This confirms that the oil combustion-industrial factor was likely associated with multiple sources and the values observed downwind of harbour appear to be influenced by heavy oil combustion in ship's engine. Lower ratios than 2 were commonly associated with atmospheric pollution source such as thermal power plant or oil refinery [8]. Ratios approximately equal 0.5 are typically found in diesel combustion particles from road traffic [6, 10].

The city of Rijeka (latitude 45°21'N, longitude 14°26'E) is not a typical example of a highly polluted urban area. It is the largest Croatian port and the third city by size in the Republic of Croatia with approximately 130,000 inhabitants. The current cargo traffic in the port of Rijeka is of moderate intensity with approximately 10 Mt/year. At the same time, the harbour throughput is approximately 190,000 containers and 170,000 passengers per year [11].

During three years sampling period (24th February 2012 - 2th June 2015) 321 daily $PM_{2.5}$ samples were collected. Samples were analyzed with X-ray Fluorescence (XRF) and Laser Integrated Plate Method (LIPM). The results obtained were statistically evaluated using Positive Matrix Factorization (PMF) with the intention to identify contributing of ship emission to the fine particle emission. The focus of the study is to distinguish ship emission from the other anthropogenic contributions such as emission from thermal power plant, oil refinery, biomass burning and road traffic. The default objectives are to identify the contribution of in-port ship emissions to $PM_{2.5}$ fraction and characterization of this source.

The impact of these components varies a lot depending on the meteorological conditions. Average daily wind speed in sampling period was relatively low, averaging at the 1.2 m/s [12], which often caused accumulation of air pollution in the Kvarner Bay.

2. Experimental

2.1. Sample collection

As the intention was to identify fingerprints of the ship emission in the city of Rijeka, our sampling site was located in the Port of Rijeka (Fig. 1), close to the main bus stop (50m) and two busy roads with average traffic intensity of 25 to 30 thousand cars, trucks and buses per day. The samples were collected during the three years period (from 24th February 2012 to 2th June 2015). 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 (Fig. 2). All samples were collected during 24 hours period.

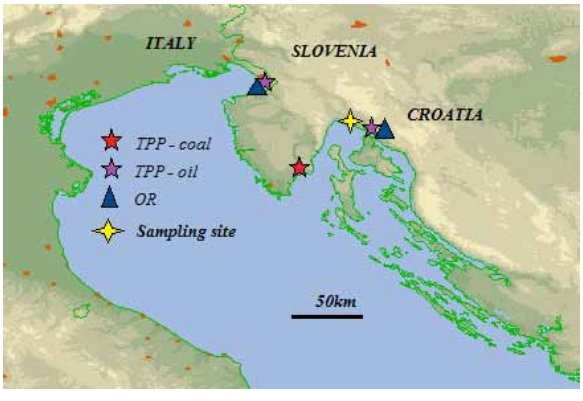

Figure 1 Location of sampling site in Rijeka, thermal powered plants (TPP – oil; TPP - coal) and oil refinery (OR)

A cyclone sampler 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. This airflow rate was chosen to ensure that the cut-off size of particulate matter is 2.5 μm. At the same time the areal density of collected material is very similar to the one that would be obtained with the prescribed Reference Method as defined by the European Standard [13]. In total, 321 samples were collected.

The total $PM_{2.5}$ mass has been 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 at the Australian Nuclear Science and Technology Organization [14].

Figure 2 Air sampler for $PM_{2.5}$ fraction positioned at Port of Rijeka

2.2. Analysis

All fine aerosol samples were analyzed by a nondestructive XRF and LIPM techniques at the Laboratory for elemental microanalysis (LEMA) in Department of Physics University of Rijeka.

For the XRF analysis, a low-power rhodium X-ray tube (by X-Ray Optical Systems, model X-Beam) was used (50 kV, 1 mA). A collimated beam with a 2 mm diameter perpendicular to the sample surface was used to scan the sample area of 8 × 8 mm^2. Characteristic X-rays were measured with a thermoelectrically cooled silicon drift detector Amptek X-123SDD (energy resolution of 142 eV for Mn-Kα line) positioned at 45º relative to the sample normal (Fig. 3). The samples were irradiated for 3600 s. With this technique performed in the air we can detect the following most commonly occurring elements: Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr and Pb**.** Quantitative analysis was obtained by means of the software package Quantitative X-ray Analysis System developed by the International Atomic Energy Agency [15]. Relative error includes the system calibration error and spectrum fitting error. Relative errors for XRF concentrations for major elements were from 6.2% (S) to 7.3% (Zn) and for minor elements were from 12.6% (Cu) to 37.4% (P). Additionally, black carbon (BC) was measured using the Laser Integrating Plate Method (LIPM) assuming a mass absorption coefficient of 7.02 m^2g^{-1} for the laser beam wavelength of 633 nm [16]. Relative error for BC concentrations was 8%. More detailed description of the set-up used is given in our recent reference [17].

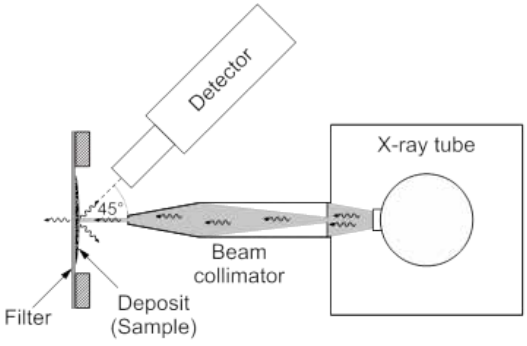

Figure 3 Diagram of the XRF setup at LEMA Department of Physics, Rijeka

3. Results

For XRF technique, the minimum detection limits of surface concentration (MDL_s) were calculated by using the following equation:

$$MDL_s = \frac{3\sqrt{A}}{ItK}$$

where A_B stands for background counts in ±3σ region below the $K\alpha$ X- ray line, K - sensitivity, I is the X-ray tube current and t is the irradiation time. The minimum detection limit of the volume concentration (MDL) was obtained as

$$MDL = MDL_s \frac{S}{V}$$

where S is the filtration surface area, and V is the sampled air volume.

For XRF technique minimum detection limits (MDL) of elements from Al to Pb are in the range of 0.6 to 22 ngm^{-3} (Fig. 4). For this work important are MDL(V) and MDL(Ni) which are 0.75 and 0.6 ngm^{-3} respectvely.

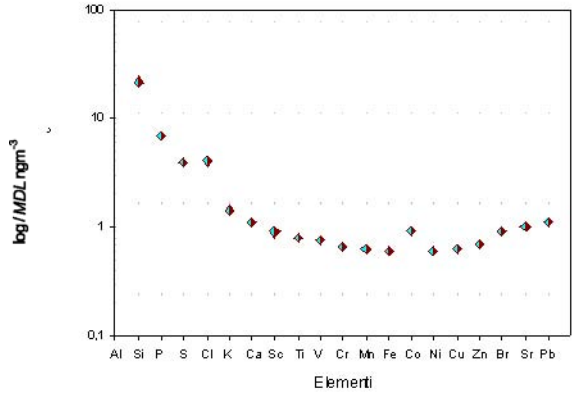

Figure 4 Minimum detection limits (MDL) of XRF technique

Overall relative errors for concentrations of V and Ni are 13.1% and 15.7% respectively. In the Table 1 we presented average daily concentrations for elements characteristic for oil combustion such as S, V and Ni, number of samples collected in corresponding year, number of samples with V/Ni ratio higher than 2.5, and throughput in Port of Rijeka for 2012-2014. The throughput in Port increases by years, especially the throughput of containers [18]**.** Conversely, averages of daily concentrations of S, V and Ni decrease. As can be seen, daily concentrations of Ni increases in 2015 by 50% compared to the daily concentrations in last year. Increases of Ni are connected with emission of heavy oil combustion in oil refinery and thermal power plant [8]. During the entire sampling period, we had only 49 days with V/Ni ratio higher than 2.5. When we used only these days in calculation, average V/Ni ratio is 3 ± 0.4, with minimum of 2.6 and maximum of 5.5. For these days it was obvious that emission from ships was present in the the fine air pollution fraction.

Table 1 Average concentration of elements in ngm^{-3}. N is the number of sampling days, and N(V/Ni>2.5) is the number of days with characteristic V/Ni ratio for ship emission. Additionally, we added throughput in Port of Rijeka (total cargo, containers and passengers)

		2012	2013	2014	2015
c / ngm-3	S	1200 ± 580	730 ± 490	860 ± 550	680 ± 470
	V	9.1 ± 7.0	4.3 ± 3.2	2.9 ± 2.1	2.3 ± 5.3
	Ni	3.5 ± 2.9	2.2 ± 2.9	1.8 ± 1.3	3.8 ± 3.7
%	(V/Ni>2.5)	39	11	18	9
Total	m /Mt	8.6	8.7	9	
	containers	152016	169943	192004	
	passangers	169190	173062	159607	

In Fig. 5 XRF spectrum for sample collected on 22 March 2014. This spectrum represented emission of fine particle from several sources. The results of quantitative analysis show that for this sample V/Ni ratio equals to 3 which indicates the presence of ship emission.

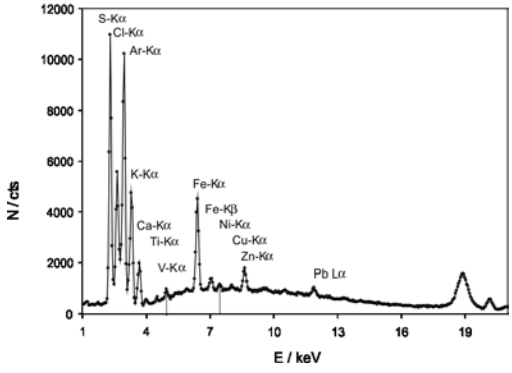

Figure 5 Representative XRF spectrum of PM2.5 fraction on 22 March 2014 connected by "ship emission" one of the pollution sources

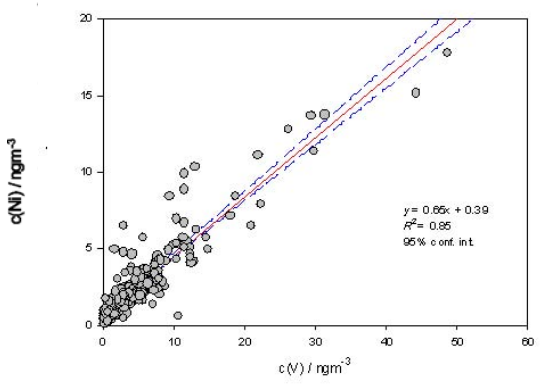

Figure 6 Nickel vs. vanadium plot in fine fraction of aerosols in Rijeka from 2012 to 2015

In Fig. 6 are shown correlation between all concentrations of V and Ni. It is obvious that V and Ni sampled in Port of Rijeka have several sources such as diesel engines (trucks, buses, etc.), heavy oil combustion (thermal power plant, oil industry, etc.) and ship emission. To separate source "ship emission" from the other sources of V and Ni, we used positive matrix factorization (PMF). This method is the most commonly used statistical method which is very effective in solving environmental problems such as identification of natural or anthropogenic sources. More details for PMF method are in literature [19, 20, 21].

In Table 2 we presented average source contribution to the total fine mass. The major contributions to the fine mass were coming from different sources, such as auto, biomass burning and secondary sulphate.

Table 2 Average source contribution to the total fine mass given in percentages

Source	**% Mass**
Auto	27 ± 5
Biomass burning	21 ± 3
Secondary sulphate	17 ± 3
Road dust	12 ± 3
Industry iron	11 ± 3
Ship emission	10 ± 2
Soil-event	1.5 ± 1.4

Source named "auto" included particulate matter from exhaust, tire and brake wear. This source is dominated by BC, Fe and S with traces of Cu, Zn, Pb, K, Si, P, Cr, V and Ni. The emission of Fe is typical indicator of engine wear. Elements such as, Cu and Zn indicate breaks and tire ware, respectively. In this factor average V/Ni ratio is 0.9, which is typical for diesel engine combustion [6] such as trucks, tractors and other transport vehicles used for in-port transport.

Source named "biomass burning" is dominated by K and BC [22] with traces S, Fe, Zn and Pb. This source is shown wood burning in domestic heating for winter period.

Source named "secondary sulphate" is dominated by S with traces of BC, K, Si and Ca. This source is correlated by industry [23, 24]. The major industrial complex comprising of 320 MW oil powered thermal plant (TPP) and the oil refinery which are both located 9 km eastward from the city centre. Other possible pollution sources are a coal powered thermal plant of 330 MW located at the Port Plomin (30 km southwest from Rijeka) and an 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).

Source named "road dust" is dominated by BC and Ca with traces of S, Fe, K, Si and P [25]. Calcium is from natural and anthropogenic origin, 57% of Ca belongs to calcium carbonate and 3% of Ca belongs to calcium phosphate. Calcium phosphate is a fertilizer that is occasionally offloaded in the Port of Rijeka. So, in this factor are present elements from both, natural (Si, Ca, Fe) and anthropogenic sources (P, S, Cu, Zn, BC).

Source named "industry iron" is dominated by BC, Fe, Mn, K, Ca and Zn. Atmospheric Mn, Fe, Cu and Zn are typically derived from steel industry [26]. Three km west to our sampling site is one of the largest Croatian shipyards which is most likely source of this factor.

Source named "soil event" has main constituents Si, K, Ca, Ti and Fe. We calculated Si/Fe and Ti/Fe ratio and they are 4.8 and 0.12, respectively. These ratios are characteristic for quartz rocks [10]. These rocks are not typical for our region and the event is therefore named "soil event".

Source named "ship emission" is mainly composed of BC and S with traces of K, V, Fe, Cl, Br Pb and Ni. In Fig. 7 are shown relative contributions of elements of the source. Concentrations of BC are ten (compared to conc. of sulphur) or more times higher than concentrations of other elements in this source. Therefore, concentrations of BC are normalized to 1, and other concentrations of elements to concentrations of BC. Dominant element in this source is sulphur which was present 8% of the total measured concentrations. Vanadium and nickel are present with 82% and 64% of their total measured elemental concentrations, respectively. They are found to be highly correlated with r = 0.98 (Fig. 8). Average V/Ni ratio in this source is found to be 3.1 [8, 9]. This source contributed by (10 ±2) % to the fine mass.

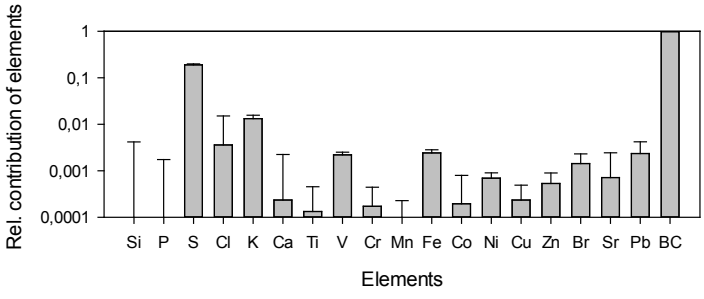

Figure 7 Relative contribution of the elements of the source named „ship emisson"

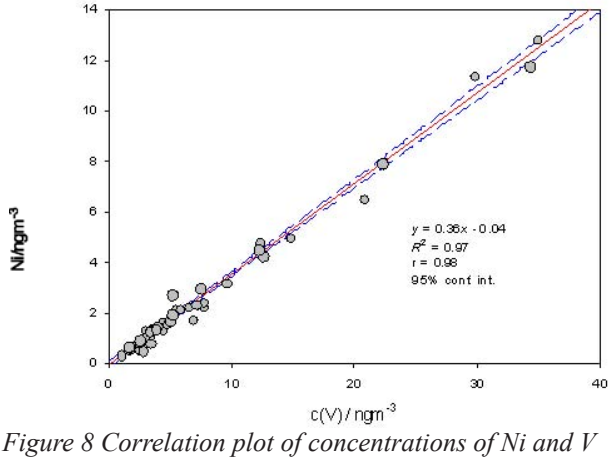

Figure 8 Correlation plot of concentrations of Ni and V in the source named „ship emission"

4. Conclusion

Harbours are important for economic and social development of coastal areas but they also represent a significant source of anthropogenic air-pollution. To identify and characterize sources of fine fraction of aerosols coming from ship emission we collected over 300 fine aerosol samples ($PM_{2.5}$) during the three years sampling period (24th February 2012 - 2th June 2015). Samples were analyzed with XRF and LIPM techniques. Concentrations of 18 elements from Si to Pb plus component BC were obtained. The results were statistically evaluated using PMF method with the intention to identify contribution of all major fine air-pollution sources including the ship emission.

The results of this study showed that the ship emissions in Rijeka contributed by 10% which is not negligible comparing to the air pollution coming from all other major industrial sources and road traffic. Statistically determined source "ship emission" is represented by S and BC with traces of K, V, Fe, Cl, Br Pb and Ni. Correlation between concentrations of V and Ni is very high with coefficient $r = 0.98$.

For ship emission, the characteristic value of V/Ni ratio did not decrease during the three years period. Average V/Ni ratio was 3 ± 0.4 with minimum of 2.6 and maximum of 5.5.

Acknowledgement

The authors are grateful to Mr. V. Mezak from the Port of Rijeka Authority and Mr. D. Mlinek from the National Meteorological and Hydrological Service for their contribution to this work.

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(Endnotes)

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Emisija aerosola s brodova u luci Rijeka, Hrvatska

Sažetak

Negativan utjecaj emisije čestica s brodova jedan od manje istraženih učinaka na zagađenje zraka. Brodovi su često pogonjeni relativno starim motorima, a istovremeno koriste gorivo upitne kvalitete. Takvi uvjeti doprinose porastu zagađenja zraka u lukama. Omjer V/Ni veći od 2,5 dobar je pokazatelj izgaranja teškog plinskog ulja s brodova. Da bi istražili taj doprinos zagađenju zraka u Luka Rijeka izmjerili smo koncentracije vanadija i nikla u finoj frakciji aerosola ($PM_{2,5}$).
Tijekom četiri godine (veljača 2012 – svibanj 2015) prikupljeno je više od 300 uzoraka fine frakcije aerosol ($PM_{2,5}$). Uzorci su analizirani pomoću dviju metoda; flourescencije X-zraka i apsorpcijske metode određivanja crnog ugljika u Laboratoriju za elementnu mikroanalizu pri Odjelu za fiziku Sveučilišta u Rijeci. Određene su koncentracije 18 elemenata od Si do Pb kao i komponenta crni ugljik (BC). Rezultati su statistički obrađeni pomoću pozitivne matrične faktorizacije.
Godišnji omjeri V/Ni iznose 3 ± 0,3 te ne pokazuju padajući trend. Statistički određen izvor "emisija brodova" čine glavne komponente kao S, Na, K, V, Ni i BC. Ovaj izvor umjetnog porijekla čini 10% od ukupne mase $PM_{2.5}$.

Ključne riječi: $PM_{2,5}$, emisija brodova, vanadij, nikal, V/Ni