

Environmental Pollution and Ecosystem Surveys in Rijeka-Bakar, Croatia - A Review

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Summary

Rijeka and Bakar are historically industrial areas of Croatia and as such suffer greater risk of soil, water and air pollution. The aim of this review paper was to describe the specific industrial history of this area, to give an overview of the relevant soil, water, sediment and air pollution-related research over the past few decades, with an emphasis on soil contamination, and finally, to determine the need of comprehensive environmental monitoring of the Rijeka-Bakar area. Overall, historically polluted sites and the pending disposal of hazardous waste in the area present a potential threat to the environment, and a comprehensive soil, water and air monitoring program would be advisable. Most recent soil surveys indicated that Pb, Zn and Hg concentrations exceed the limit values for industrial and commercial use in industrialized areas on occasion, therefore, heavy metals monitoring would prove beneficial for soil protection and management. The decrease of the industry had ultimately resulted in better air quality in Rijeka-Bakar area. Due to future predictions of increasing O₃ levels on a global scale, monitoring of this air pollutant is greatly encouraged.

Key words

soil, water, sediment, air pollution, biological magnification

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Introduction

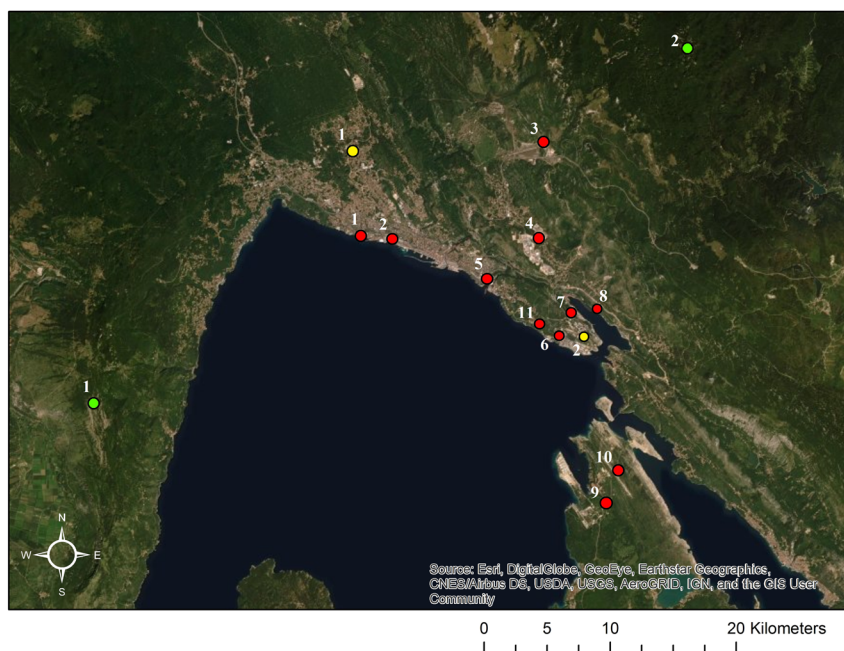
The town of Bakar is located on the northern Croatian Adriatic coast in Primorje-Gorski Kotar County, about 10 km southeast from Croatia's main port and third largest city - Rijeka, which resulted in shipbuilding and maritime transport in that entire area. Rijeka is well connected with the whole Europe through railways, roads and air connections.

The Bakar Bay contains Bulk Cargo Terminal of the Port of Rijeka, handling coal and iron ore cargo and used to be known for its industrial complex that included a coke factory which operated between 1976 and 1995 and produced considerable amount of air pollution. In the hinterland of Bakar Bay there is the industrial zone Bakar and Grobnik racetracks and airport. In Rijeka there are two shipyards, "Viktor Lenac" and "3. Maj" and a closed oil refinery INA d.d. - Mlaka which is due for remediation since its closure in 2008 (Pajić and Glavan, 2011; Valerjev Ogurlić, 2016).

Just 2 km southwest from Bakar, in Kostrena Municipality, there is an operating oil refinery INA d.d. – Urinj, thermal power plant Rijeka, and further south, on the Island of Krk, Rijeka Airport and DINA Petrochemical plant are located (Figure 1). Thermal power plant Rijeka and DINA petrochemical plant are inactive for several years (2015).

During the late sixties and seventies the City of Rijeka and its surroundings underwent rapid industrialization that resulted in high air pollutants emissions originated from the industry and transportation in the whole area. Since the nineties, after wartime (1991-1995), the emissions diminished and never recurred in that extent, as it was confirmed by various studies over the past decades (Alebić-Juretić and Arko-Pijevac, 1989; Alebić-Juretić, 1995, 2005, 2011a, 2017; Picer et al., 1978; Picer and Picer, 1992; Picer, 2000).

Today, the area of Rijeka-Bakar can be described as a high pollution risk area, considering how the plans for growth in the industrial zone Bakar (Gašpert, 2017), traffic increase in Rijeka Airport (Glavan, 2016) and future LNG import terminal for receiving, storing, reloading and regasification of liquefied natural gas (LNG Hrvatska d.o.o., 2019) could result in the potential increase of emissions in the near future. But not all increase of environmental problems in the area could be caused by the growth of industry, seeing how the insolvency of DINA Petrochemical Company and its winding-up proceedings (Paparella, 2017; Antešić, 2017) may lead to delays in the disposal of both hazardous and non-hazardous waste that had been produced there.



Legend

POLLUTERS ●	LANDFILLS ●	PROTECTED AREAS ●
1. Shipyard "3.Maj"	1. Jama Sovjak	1. Nature Park Učka
2. Oil refinery INA d.d. – Mlaka plant (CLOSED)	2. Šoići	2. National Park Risnjak
3. Racetracks and airport Grobnik		
4. Industry zone d.o.o. Bakar		
5. Shipyard "Viktor Lenac"		
6. Oil refinery INA d.d. – Urinj plant		
7. Coke plant Bakar (CLOSED)		
8. Bulk Cargo Terminal		
9. DIOKI d.d. – Organic Petrochemical Company (CLOSED)		
10. Rijeka Airport		
11. Thermal power plant Rijeka (CLOSED)		

Figure 1. Map of point source polluters in Rijeka-Bakar area (Map produced using ArcGIS® software by Esri. Copyright © Esri. All rights reserved. Edited by Iva Hrelja, 2019)

Croatian Agency for Environment and Nature published in 2018 a "Report on data from the registry of facilities where dangerous substances are present", which identifies facilities that pose a risk of a potential or increased risk of domino effect with respect to the quantity reported and the category of dangerous substances. Primorje-Gorski Kotar is the leading county in total quantity of dangerous substances in Croatia (2 347 384.21 t) and it is followed by Sisak-Moslavina (1 367 393.39 t), and Zagreb, the country's capital (176 622.44 t) (HAOP, 2018). The disposal of these dangerous substances could prove to be an environmental problem in the future. Until recently, besides landfills for municipal waste in the area, there were also three landfills for industrial waste. Landfill Šoići for non-hazardous industrial waste is currently active and under the management of INA d. d, but up for closure and clean-up in the near future (Knežević et al., 2017). DINA Petrochemical plant used its own non-hazardous industrial waste landfill and exported its hazardous waste to Kutina, some 240 km northeast from the island of Krk (Poslovni dnevnik, 2015, 2016). The company is not operational anymore and the fate of its waste is still uncertain (Antešić, 2017). The hazardous waste of the Rijeka-Bakar area was being disposed of in a karst pit "Jama Sovjak" from 1955 to 1990 (Ribić, 2008). It presents a potential source of groundwater pollution, but its clean-up is still pending to this day (Petrak, 2016). It is worth noting the proximity of the industrialized Rijeka-Bakar area to Croatia's protected locations: Nature park Učka to the southwest (SW) and National Park Risnjak to the northeast (NE). These two protected locations are on the path of two prevailing air streams in this region that move from NE and SW (Šinik et al., 1994). There are several studies on heavy metal pollution and impacts of acid rain in National Park Risnjak that showed an increased amount of lead (Pb) and cadmium (Cd) in the soils of this National Park (Vrbek and Buzjak, 2004; Vrbek and Gašparac, 1992; Vrbek et al., 1991; Miko et al. 1999b) as well as increased amount of Pb in Nature park Učka (Jakovljević et al., 2016). However, no connection between the industry of Rijeka-Bakar area and accumulation of Pb and Cd has been found in these studies. Rijeka-Bakar area is also located in the karst region of Croatia which increases the danger of potential pollutants to percolate underground and compromise the groundwater (Cuculić, 2012; Picer, 2005; Prohić et al., 1997; Miko et al., 1999a, 2000). Karst areas are more susceptible to environmental pollution than other terrains because the natural treatment of water-borne contaminants is mostly ineffective due to poor physical filtration of shallow soils and because of rapid infiltration which disables the evaporation of volatile organic compounds (Ford and Williams, 1989).

Soil

Soils are taken for granted by the majority of the human population, but they are in fact the foundation for growth and development of every country on Earth and are an extremely important component of the environment. Soils can be observed to have a complex structure, with unique biological, chemical and physical characteristics. The greatest role is in food production; they support plants, the primary producers, and supply them with moisture and nutrients, so providing all other terrestrial ecosystems with the basis of the food chain. Soils are under considerable threat from pollution (FAO and ITPS, 2015) and yet, the least research was done precisely regarding this issue in

Rijeka-Bakar area. The limiting factor for the development of monitoring programs and projects for sustainable soil and land management is the absence of legislation that would provide limit values of pollutants for different land uses in Croatia, and so researchers (Bašić and Kisić, 1995; Bogunović, 1996; Kisić et al., 2008a, 2008b) involved in soil surveys in Rijeka-Bakar area compared their conclusions of the state of the soils in the area to neighboring countries in the European Union (Table 1). The only legislation for limit values in Croatia exists for agricultural use, as shown in Table 2.

Table 1. Tolerance limit values for industrial and commercial land use in Germany, Italy and Slovakia

Metals	Germany	Italy	Slovakia
	mg/kg d.w.		
Cd	60	15	20
Hg	80	5	10
Pb	2000	1000	600
As	140	50	50
Cr	1000	15	800
Ni	900	500	500
Zn	-	1500	3000
Co	-	250	300
Mo	-	-	200
Cu	-	600	500
Ba	-	-	2000
V	-	250	500

Source: Kisić et al., 2008a

Table 2. Tolerance limit values for agricultural land use in Croatia

Metals	soil pH in 1M KCl		
	<5	5-6	>6
Cd	1	1.5	2
Cr	40	80	120
Cu	60	90	150
Hg	0.5	1	1.5
Ni	30	50	75
Pb	50	100	150
Zn	60	150	200
Mo	15	15	15
As	15	25	30
Co	30	50	60

Source: Narodne novine, 2019

In 2009, a Geochemical Atlas of the Republic of Croatia was published (Halamić and Miko, 2009) representing the natural spatial distribution of chemical elements in surface soils of Croatia, which, as the authors note, should be the basis for the adoption of any regulatory provisions. In this review we compared the Atlas values of potential toxic elements to the results of relevant studies in Rijeka-Bakar area (Table 3), two of which had been done by the same group of scientists, on two different locations - closed oil refinery INA d.d. – Mlaka (Kisić et al., 2008a) and an operating oil refinery INA d.d. – Urinj (Kisić et al., 2008b). The third study also included INA d.d. – Urinj location, with addition of multiple others in Primorje-Gorski Kotar County, such as Bakarac Village and Crno Village once covered with vineyards (Bašić and Kisić, 1995).

Table 3. The range from lowest to highest recorded values of heavy metals in Mlaka and Urinj plants compared to median values for coastal Croatia

Metals	Coastal Croatia	Mlaka	Urinj
	mg/kg d.w.		
Cd	1.1	< 0.1 *	<0.3-2.1
Hg	0.08	<0.1-10.0	0.02-4.00
Pb	48.7	24-1083	15-788
As	18	12-80	3.6-35.4
Cr	121	9-104	10-126
Ni	74.6	15-81	20-126
Zn	108	98-1760	42-1620
Co	18	27-39	6-28
Mo	nd	0.08-11	0.4-86.2
Cu	35.5	25-307	16-368
Ba	297	39-705	258-362
V	148	32-136	21-196

Source: Kisić et al., 2008a, 2008b; Halamić and Miko, 2009;

* <0.1 mg/kg = LOD = limit of detection; nd = no data

Besides giving an overview of soil types and heavy metal concentrations in the greater County area, Kisić et al. (2008a, 2008b) measured concentrations of PAHs (Polycyclic aromatic hydrocarbons), heavy metals, total and mineral oil concentrations at the two mentioned locations, as well as changes in basic soil chemical parameters (soil pH, organic matter content, plant available phosphorous and potassium, total carbon, nitrogen, hydrogen and sulphur content as well as changes in C:H:N:S ratio in the soil) in locations within and outside the refinery circle (approximately 2 km from the refinery). Bašić and Kisić (1995) investigated only heavy metal concentrations in soil in the greater Primorje-Gorski Kotar County.

Bašić and Kisić (1995) concluded that Ni content in all analysed soils was at least increased or that the contamination with this metal is high (e.g., in Urinj Plant 53 mg/kg, in Rijeka 38 g/kg and in Bakarac 50 mg/kg was found). In the investigated sites

Mo and Hg did not appear in relevant quantities and Cd, Cu and Pb were the leading soil pollutants in the County. In Urinj Plant 0.87 mg/kg of Cd, 107 mg/kg of Cu and 150 mg of Pb was found, in Rijeka 1.02 mg/kg of Cd, 154 of Cu and 350 mg/kg of Pb and in Bakarac 1.9 mg/kg of Cd, 39 mg/kg of Cu and 63 mg/kg of Pb was found. They observed that the concentrations of pollutants emitted from the former coke plant in Bakar are low in the vicinity of the plant, and that their content is increased in the soils where pollution deposition occurs, i.e., the increased content of Cu, Ni, Kr, V and Zn was observed in soils approximately 5 km east of the plant. They offered a possible explanation for this – the increased content of these heavy metals could be attributed to the strong winds in the area, where air streams from NE and SW prevail (Šinik et al., 1994).

Bogunović (1996) in his overview of Croatian agricultural soils also briefly referred to Rijeka – Bakar area regarding Ni, Co and Cd concentrations and concluded that 60 mg/kg of Ni was found in the vicinity of the former coke plant, 75 mg/kg of Cu in INA d.d. – Urinj and 1 mg/kg of Cd in the soils of the Village of Bakarac and the City of Rijeka. No contamination of agricultural soils was recorded.

In a closed oil refinery INA d.d – Mlaka (Kisić et al., 2008a), PAH concentrations were measured at 15 investigated locations in the soil and were at background values or below tolerance level for the sum of PAHs, which amounts to 60-120 mg/kg. The mentioned limits were also taken from neighbouring countries legislations and refer to the industrial and commercial land use (Kisić et al., 2008a). The increase in total and mineral oils was not recorded. Three of twelve investigated heavy metal concentrations (cadmium - Cd, mercury - Hg, lead - Pb, copper - Cu, cobalt - Co, molybdenum - Mo, barium - Ba, vanadium - V, arsenic - As, chrome - Cr, nickel – Ni and zinc - Zn) exhibited an increase around or above tolerance levels; Pb, Zn and Hg. The highest concentration of Pb at Mlaka Plant was 1083 mg/kg d.w. (d.w.: dry weight of soil). Tolerance limit values for Zn in Germany do not exist but in Italy they are 1500 mg/kg d.w. The highest concentration of Zn found at Mlaka Plant was 1760 mg/kg d.w. For Hg maximum concentration found at Mlaka Plant was 10 mg/kg d.w. The overall most polluted sample site was found to be at the gas flame torch.

In an operational oil refinery INA d.d. – Urinj, the sum of PAHs at 32 investigated locations were also found to be at background values or below tolerance levels (80 mg/kg for total PAHs; Kisić et al., 2008b), but the results also revealed the need for monitoring of the central waste pit located within the refinery, where solidified waste is being disposed of and which showed increased concentrations of anthracene, phenanthrene, pyrene and fluoranthene (although still below tolerance levels). Total and mineral oils were not recorded on all sites, with an exception of one – the central waste pit, where significantly increased amount was found. Tolerance limit value for total oils is 10 g/kg for industrial and commercial land use (Kisić et al., 2008b) and the concentrations found were 56.102 g/kg for total oil, and 29.192 g/kg for mineral oils in the 0-10 cm layer of soil. When it comes to investigated heavy metal concentrations (Cd, Hg, Pb, Cu, Co, Mo, Ba, V, As, Cr, Ni, Zn), only Cd, Cr, Co and V didn't show a significant increase in their concentrations in all sample locations. The most problematic heavy metals found in concentrations

around or above limit values were again Pb, Zn and Hg with the highest values of 788 mg/kg d.w., 1620 mg/kg d.w. and 4 mg/kg d.w. of soil, respectively. Table 3 shows the range from lowest to highest recorded concentrations of investigated heavy metals in both INA d.d – Mlaka and INA d.d. – Urinj plants. These values are compared to median values for coastal Croatia which can be found in the Geochemical Atlas of the Republic of Croatia (Halamić and Miko, 2009). The table confirms the previous findings of Pb, Zn and Hg as heavy metals with above average concentrations in this area and could be the focus of future studies.

Water

The Gulf of Rijeka is a landlocked area that covers 450 km², with an average depth of 60 m and volume of 27 km³ (Bihari et al., 2007) with a number of previously mentioned industrial enterprises located along its coastline. Therefore, an increase in anthropogenic influence on the marine environment is to be expected. The sea currents in the Gulf of Rijeka are very weak and the aquatic system behaves as an essentially closed system with slow exchange of water masses (Jakšić et al., 2005). It is for that reason that all of the studies of industrial pollution done in this area resulted in heterogenic results for seawater samples. A study done by Bihari et al. (2004) defined five classes of seawater quality, and so areas were ranked in five categories (excellent, good, fair, poor and very poor) according to their potential toxic influence. The water quality of selected sites in the Gulf of Rijeka were described as good quality, occasionally stressed, but they also showed a significant difference in recorded minimum and maximum levels of seawater toxicity, which means the area is often a scene of sudden and rapid changes that can lead to serious short-term contamination of the marine environment. Studies of PCBs (polychlorinated biphenyl) and DDT (dihlor-difenil-trihloretan) levels in the area had also been done (Picer, 1990, 2000; Picer and Picer 1992). They observed a substantial decline of these compounds in the last decades, which can be attributed to their legal ban in the eighties on the European Union level (Directives 79/117/EEC and 76/769/EEC).

Sediment

A substantial number of studies of the sea sediments in the area had been done throughout the years (Alebić-Juretić, 2011b; Bihari et al., 2007; Cukrov et al., 2010, 2014; Fafandel et al., 2015; Korlević et al., 2015; Linšak et al., 2012; Miko et al., 2010; Tomić Linšak et al., 2011; Traven, 2015; Traven et al., 2015). For the most part they investigated the concentrations of PAHs and heavy metals in the vicinity of shipyards and oil refineries. Bihari et al. (2007) found that the sediment samples contained PAHs of higher molecular weight compared to the majority of seawater samples, and Alebić-Juretić (2011b) had observed their declining trend at all investigated sites in the period from 1998 to 2006. Linšak et al. (2012) found high environmental risks in heavy metals concentrations, which were the highest in shipyards, but nonetheless, Cukrov (2014) found Bakar Bay to be less polluted with heavy metals than it was originally believed. Traven (2015) came to a conclusion that a low to medium eco toxic risk of marine sediment exists.

Air

In Rijeka-Bakar area the oil refinery, airport, electric power plant and traffic are all sources of pollution and air quality is often the first environmental component to be compromised by their emissions. The hazardous air pollutants that compromise air quality are particulate matter (PM), nitrogen oxides (NO_x), carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs), BTEX compounds (benzene, toluene, ethylbenzene and xylene), hydrogen sulphide (H₂S), sulphur dioxide (SO₂) and ozone (O₃). The air quality monitoring programme started in mid-seventies in the Rijeka Bay area (Matković and Alebić-Juretić, 1998) and from that time various studies had been done in order to monitor the movements of these compounds in the atmosphere (Alebić-Juretić, 1994, 1995, 2001, 2005, 2008, 2011a, 2011b, 2012, 2015; Alebić-Juretić and Arko-Pijevac, 1989, 2005; Alebić-Juretić and Šojat, 1998; Alebić-Juretić and Matković, 2000; Alebić-Juretić and Mićović, 2005; Alebić-Juretić et al., 2009; Alebić-Juretić and Mifka, 2017; Ivošević, 2014; Ivošević et al., 2016; Jelić and Bencetić Klaić, 2010; Matković and Alebić-Juretić, 1998; Mićović et al., 2010; Prtenjak et al., 2009; Šinik et al., 1994). All of them agree that the highest emissions in the area occurred during the seventies and eighties of the 20th century and, due to reduced industrial activity and improved quality of fuel since the nineties, air pollution in the area was significantly reduced. Figure 2 is based on the data from Alebić-Juretić (2011a) and shows the annual mean concentrations of SO₂ and black smoke in the City of Rijeka for the period from 1986-2009. The declining trend is visible in Figure 2.

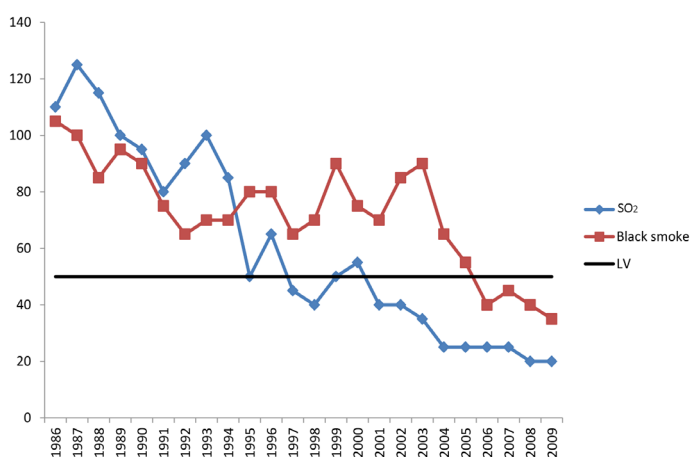


Figure 2. Annual mean concentrations of SO₂ and black smoke in the City of Rijeka. LV = limit value (50 µg/m³). Values based on data from Alebić-Juretić, 2011a

Alebić-Juretić (2011a) also reported the annual mean concentrations of H₂S, PM, NO₂ and O₃ in the City of Rijeka. The author noted there was no trend in H₂S regarding the annual means which ranged from 0.9 - 3.5 µg/m³ (limit value - LV is 2 µg/m³) for the period from 1986-2009. Although the annual means of PM measured from 2003-2009 were around limit value - LV (50 µg/m³), the number of exceedances was 2 - 3 times higher than allowed per year (35 times). The decline of exceedances of PM started in 2007, which was attributed to introduction of natural gas in the city center. Mean annual values for NO₂ in the period from 1986-1997 were continuously above LV (40 µg/m³) with a peak around 55 µg/m³ in 1990. From the period of 1997-2009 the mean annual concentrations were below LV, except for 2001 when

it was around $45 \mu\text{g}/\text{m}^3$. Airborne O_3 showed a declining temporal trend in the period from 1999 - 2008 with the mean annual concentrations declining steadily from $65 \mu\text{g}/\text{m}^3$ in 1999 to $35 \mu\text{g}/\text{m}^3$ in 2008 (Alebić-Juretić, 2011a). Further analyses, however, revealed an increasing trend from 2009-2016 (Zubak et al., 2017). The increase of O_3 in the future due to climate change is to be expected on both regional and global scale (Zubak et al., 2017).

Biological magnification and human health

Biological magnification

The impact of PAHs, heavy metals and other pollutants such as PCBs and DDT on the environment can be measured by determination of DNA damage in marine organisms and many studies had been done in Rijeka – Bakar area throughout the years using the mussel *Mytilus galloprovincialis* as one of the most widely used bioindicator species, allowing the comparison of data from different studies from various locations (Bihari et al., 2007; Jakšić et al., 2005; Ozretić et al., 1990; Perić et al., 2012a, 2012b; Picer, 1991; Picer et al., 1978; Picer and Picer, 1986; Popadić et al., 2013; Rožmarić et al., 2012).

Bihari et al. (2007) found that mussels from majority of sampling sites tend to accumulate PAHs of lower molecular weight. Mussel anoxic survival was influenced by the presence of complex mixture of toxic contaminants, not only PAHs. The relationship between PAH contents in different marine matrices and their ability to affect mussels revealed specific interactions between an organism and complex mixture of toxic contaminants present in the marine environment. Popadić et al. (2013) studied the heavy metal concentrations in the area and found that they generally fall into allowed depositional values for marine environments; only the area in front of the former coke plant and the City of Bakar harbour was heavily polluted.

Human Health

Pollutants in the air, water and soil affect human health. For instance, numerous studies have been done on global and regional scales to estimate premature mortality associated with SO_2 , PM and O_3 pollution (Pandey et al., 2005; Ghude et al., 2016). During the period of high air pollution in Rijeka – Bakar area in the eighties three relevant studies were conducted to estimate the air pollution effect on human health. The first of this study conducted by Bartoniček-Brgić and Matković (1989) investigated occurrence of respiratory diseases among preschool children in the City of Rijeka and its suburban communities affected by air pollution from SO_2 and black smoke. The city center suffered the highest air pollution with annual means twice as much as WHO guideline values for SO_2 and black smoke (Figure 2). The incidences of overall acute respiratory diseases, acute diseases of lower respiratory system and acute non-obstructive bronchitis were in correlation to black smoke ($p < 0.05$) and the incidence of non-obstructive bronchitis correlated also with ambient SO_2 concentrations ($p < 0.05$). The second study was conducted by Matković et al. (1998). It investigated disorders of ventilatory function in unemployed nonsmoking women living in areas with different air pollution in Bakar, Krašica and Viškovo during the period from 1986 - 1990. The control group had lived in the Viškovo area where measurements showed the air to be clean (SO_2

concentrations were constantly below $50 \mu\text{g}/\text{m}^3$). Continuous air quality measurements showed that SO_2 concentrations exceeded the recommended values in Bakar and Krašica. Mean annual SO_2 concentrations in Bakar ranged from $67 - 74 \mu\text{g}/\text{m}^3$ and in Krašica from $50 - 79 \mu\text{g}/\text{m}^3$. Women of Viškovo manifested significantly better values of ventilatory function than the women living in Bakar. They concluded that the decreased ventilatory function in the Bakar and Krašica women may have been associated with long-term exposure to increased air pollution.

The third study was conducted by Alebić-Juretić et al. (2001) in the period from 1987-1996. They investigated the effect of air pollution (SO_2) and how it might have contributed to an increased risk of preterm delivery in the City of Rijeka. They found an 11% increase in the risk of preterm delivery among mothers who were resident in the city, compared to the mothers in the region (where concentrations of SO_2 were below $40 \mu\text{g}/\text{m}^3$). They concluded that the socio-demographic factors such as education, maternal age, marital status and smoking habits could not account for this increased risk, via the Breslow-Day test for homogeneity of the common odds ratio, and they considered the elevated ambient air pollution as a possible cause.

Another study published by Alebić-Juretić et al. (2007) investigated if increased PM and O_3 levels could have caused an increase in mortality in Croatia during the 2003 heat wave (August 8 - 13th). The study was conducted in the cities of Zagreb and Rijeka. The average concentrations of PM and O_3 during this period were 74.0 ± 20.3 in Zagreb and $83.8 \pm 5.9 \mu\text{g}/\text{m}^3$ in Rijeka, respectively. They estimated approximately 30-60 excess deaths due to the combined effects of PM and O_3 .

Conclusion

Although the peak of industrial environmental pollution had long passed in Rijeka-Bakar area, a comprehensive soil, water and air monitoring program would be useful in a broader context of environmental safety in the area. Current plans for growth in the industrial zone Bakar and traffic increase in Rijeka Airport could lead to growing emissions and air pollution in the future. Additionally, perhaps even more than the growing industry, historically polluted sites (the previously mentioned karst pit “Jama Sovjak”, landfill Šoići, closed oil refinery INA d.d. – Mlaka) and the disposal of hazardous waste produced in the area over the decades may prove to be of greater importance, seeing how their remediation is not only pending but highly necessary. The soil surveys conducted in the area throughout the years show the need for continuous monitoring of Pb, Zn and Hg, seeing how the average concentrations in industrialized areas of Mlaka and Urinj plants exceeded the limit values for industrial and commercial use. The aquatic system of the Gulf of Rijeka would also benefit from a continuous monitoring plan, as it was proved to be susceptible to rapid changes and in risk of short-term contamination.

The air quality monitoring program existed in the area since the mid-seventies and due to reduced industrial activity and improved quality of fuel since the nineties, air pollution in the Rijeka-Bakar area had been significantly reduced. In terms of human health, PM and O_3 should be in the focus of air monitoring since further increase of O_3 is to be expected in the future on the global scale due to climate change.

References

- Alebić-Juretić A. (1994). Precipitation chemistry within Kvarner Bay area, Northern Adriatic (Croatia), 1984–1991. *Water, Air and Soil Pollution* 78 (3): 343-357. doi:10.1007/BF00483042
- Alebić-Juretić A. (1995). Trends in sulphur dioxide concentrations and sulphur deposition in the urban atmosphere of Rijeka (Croatia). *Water, Air and Soil Pollution*, 85 (4): 2199-2204
- Alebić-Juretić A. (2001). Airborne Ns (NO₂ and NH₃) in the Rijeka Bay Area (Croatia), 1980–1995. *The Scientific World Journal* 1 (2): 343-347
- Alebić-Juretić A. (2005). Polycyclic Aromatic Hydrocarbons and Metals in Total Suspended Particulates Collected in Rijeka, 1982-2004. Proceedings of 4th Croatian meeting Air Protection, Zadar, Croatia, September 12-16 (in Croatian)
- Alebić-Juretić A. (2008). Airborne ammonia and ammonium within the Northern Adriatic area, Croatia. *Environmental Pollution* 154 (3): 439-447
- Alebić-Juretić, A. (2011a) Air pollution and its impacts – the City of Rijeka case study. In: *Advanced Topics in Environmental Health and Air Pollution Case Studies* (Moldoveanu A., ed). InTech. doi: 10.5772/20907.
- Alebić-Juretić A. (2011b). Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998–2006. *Marine Pollution Bulletin* 62 (4): 863-869
- Alebić-Juretić A. (2012). Ozone levels in the Rijeka Bay area, Northern Adriatic, Croatia, 1999-2007. *International Journal of Remote Sensing* 33 (2): 335-345
- Alebić-Juretić A. (2015). Airborne Polycyclic Aromatic Hydrocarbons in Suspended Particulates from the Urban Atmosphere of Rijeka, Croatia. *Polycyclic Aromatic Compounds The 24th International Symposium on Polycyclic Aromatic Compounds - ISPAC 24* 35 (1): 91-101
- Alebić-Juretić A., Arko-Pijevac M. (1989). Air Pollution Damage to cell Membranes in Lichens- result of Simple Biological test Applied in Rijeka, Yugoslavia. *Water, Air and Soil Pollution* 47 (1): 25-33. doi:10.1007/BF00468994
- Alebić-Juretić A., Arko-Pijevac M. (2005). Lichens as Indicators of Air Pollution in the City of Rijeka, Croatia. *Fresenius Environmental Bulletin* 14 (1): 40-43
- Alebić-Juretić, A., Cvitaš, T., Kezele, N., Klasinc, L., Pehnc, G., Šorgo, G. (2007). Atmospheric particulate matter and ozone under heat-wave conditions: do they cause an increase of mortality in Croatia? *Bulletin of Environmental Contamination and Toxicology*, 79(4): 468-471. doi:10.1007/s00128-007-9235-2
- Alebić-Juretić A., Cvitaš T., Klasinc L. (2009). Thirty years of air quality assessments in the Bay of Rijeka, 1977-2007. In: *Proceedings of Short Papers Presented at the 7th International Conference on Air Quality - Science and Application* (Francis X. V., Khaiwal R., Chemel Ch., Newbold J., Incekic S., Kahya C. and Sokhi R. S., eds), University of Hertfordshire, Hatfield, UK
- Alebić-Juretić, A., Frković, A., Šimić, D. (2001) The Effects of Air Pollution on the Outcome of Pregnancies. *International Journal of Gynecology & Obstetrics*, 75: 315-316
- Alebić-Juretić A., Matković N. (2000). Airborne Metal Concentrations in Shipyard Environment. *Archives of Industrial Hygiene and Toxicology* 51 (2): 249-256
- Alebić-Juretić A., Mićović V. (2005). Bulk Deposition of Nitrogen within Kvarner Bay Area (Croatia), 1984-2003. In: *3rd International Nitrogen Conference* (Zhaoliang Z., Katsu M., Guangxi X., eds). Beijing, Kina, Science Press USA Inc, pp. 644-649
- Alebić-Juretić A., Miška B. (2017). Secondary Sulphur and Nitrogen Species in PM₁₀ from the Rijeka Bay Area (Croatia). *Bulletin of environmental contamination and toxicology* 98 (1): 133-140
- Alebić-Juretić A., Šojat V. (1998). Chemical composition of rainwater collected at two sampling sites in the City of Rijeka. *Archives of Industrial Hygiene and Toxicology* 49 (3): 245-250
- Antešić O. Dina starts selling land. Real estate of ex Ježić-complex up for public auction. *Novi List* [online] 2017. Available at: http://www.novolist.hr/Vijesti/Regija/Otoci/pocela-prodaja-zemljista-dine-Nekretnine-bivseg-Jezicevog-kompleksa-na-javnoj-drazbi?meta_refresh=true [Accessed June 6th, 2017] (in Croatian).
- Bartoniček-Brgić V., Matković N. (1989). Sulphur Dioxide and Black Smoke Air Pollution Impact on Incidence of Respiratory Diseases among Preschool Children in Rijeka. In: *Proceedings of the First Yugoslav Clean Air Congress, Book II: 734-747*, ISBN Zenica, Yugoslavia, June 14-16. (in Croatian)
- Bašić F., Kisić I. (1995). Soil damage in Primorsko-Goranska County, chapter in the study "Ecological and economic evaluation of the Primorsko-Goranska County for agricultural development". Study stored in a manuscript in the Fund of Professional Documentation of the Faculty of Agronomy, Department of General Agronomy, Zagreb (in Croatian)
- Bihari N., Fafandel M., Piškur V. (2007). Polycyclic aromatic hydrocarbons and ecotoxicological characterization of seawater, sediment, and mussel *Mytilus galloprovincialis* from the Gulf of Rijeka, the Adriatic Sea, Croatia. *Archives of Environmental Contamination and Toxicology* 52 (3): 379-387
- Bihari N., Mičić M., Fafandel M. (2004). Seawater quality along the Adriatic coast, Croatia, based on toxicity data. *Environmental Toxicology* 19 (2): 109-114
- Bogunović M. (1996). Soil in the Croatian agricultural area. *Agronomy Journal* 58(2-4): 99-113. (in Croatian)
- Cuculić V., Cukrov N., Omanović D., Jalžić B. (2012) Preliminary study of trace metal distribution in the water column of Urinjska špilja anchialine cave (Croatian Adriatic coast). *Natura Croatica: Periodicum Musei Historiae Naturalis Croatici* 21 (1): 28-31
- Cukrov N., Frančišković-Bilinski S., Bogner D. (2014). Metal contamination recorded in the sediment of the semi-closed Bakar Bay (Croatia). *Environmental Geochemistry and Health* 36 (2): 195-208
- Cukrov N., Frančišković-Bilinski S., Hlača B. and Barišić D. (2010). A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia, *Marine Pollution Bulletin* 62 (1): 154-167. doi:10.1100/tsw.2001.276
- Fafandel M., Piljagić J., Smodlaka Tanković M., Travizi A., Bihari N. (2015). Nutrients vs toxicity in sediments: A case study of two semi-closed basins in Rijeka Bay, Croatia. *Fresenius environmental bulletin* 24 (9a): 2888-2897
- FAO & ITPS. 2015. Status of the World's Soil Resources (SWSR) - Main Report. Rome, Italy, Food and Agriculture Organization of the United Nations and Intergovernmental Technical Panel on Soils. (also available at <http://www.fao.org/3/a-i5199e.pdf>).
- Ford D. C., Williams P. W. (1989). *Karst geomorphology and hydrology* (Vol. 601). London: Unwin Hyman.
- Gašpert S. Around 200 more employees this summer in Kukuljanovo – A kindergarten also on the way. *Novi List* [online] 2016. Available at: <http://www.novolist.hr/index.php/Vijesti/Rijeka/Na-Kukuljanovuo-od-ovog-ljeta-dvjestotinjak-zaposlenih-vise-u-zonu-stize-i-djecjivrtic> [Accessed June 6th, 2017] (in Croatian).
- Ghude, S. D., Chate, D. M., Jena, C., Beig, G., Kumar, R., Barth, M. C., Pithani, P. (2016). Premature mortality in India due to PM_{2.5} and ozone exposure. *Geophysical Research Letters* 43(9), 4650-4658
- Glavan M. Airport Rijeka introduces new air routes: increase in passenger numbers expected again this year. *Novi List* [online] 2016. Available at: <http://www.novolist.hr/Vijesti/Rijeka/Zracna-luka-Rijeka-uvodi-nove-linije-Ove-se-godine-opet-ocekuje-rast-broja-putnika> [Accessed June 6th, 2017] (in Croatian)
- Halamić J. and Miko S. (eds) (2009). *Geochemical Atlas of the Republic of Croatia*. Croatian Geological Survey, Zagreb, pp. 87.
- HAOP. Croatian Agency for Environment and Nature. Report on data from the registry of facilities where dangerous substances are present/ Evidence of reported major accidents (RPOT / OPVN) for 2017. Zagreb, 2018 (in Croatian)

- Ivošević T. (2014). Analysis of fine fraction of aerosols in Rijeka by Nuclear Analytical Techniques. PhD. University of Rijeka Faculty of Engineering (in Croatian)
- Ivošević T., Stelcer E., Orlić I., Bogdanović Radović I., Cohen D. (2016). Characterization and source apportionment of fine particulate sources at Rijeka, Croatia from 2013 to 2015. Nuclear Instruments and Methods in Physics Research. Section B: Beam Interactions with Materials and Atoms 371: 376-380
- Jakovljević, T., Radojčić-Redovniković, I., and Laslo, A. (2016). Phytoremediation of heavy metals: Applications and experiences in Croatia. *Zaštita materijala*, 57(3): 496-501
- Jakšić Ž., Batel R., Bihari N., Mičić M., Karl Zahn R. (2005). Adriatic coast as a microcosm for global genotoxic marine contamination--A long-term field study. *Marine Pollution Bulletin* 50 (11): 1314-1327
- Jelić D., Bencetić Klaić Z. Air quality in Rijeka, Croatia (2010). *Geophysical Journal* 27 (2): 147-167
- Kisić I., Bašić F., Mesić M., Zgorelec Ž., Jurišić A., Sajko K., Vuković I. (2008a). Report on the current state of contamination of the soil within the circle of the oil refinery Rijeka – Mlaka Plant. Fund of Professional Documentation of the Faculty of Agronomy, Department of General Agronomy, Zagreb (in Croatian)
- Kisić I., Bašić F., Mesić M., Zgorelec Ž., Jurišić A., Sajko K., Vuković I. (2008b). Report on the current state of contamination of the soil within the circle of the oil refinery Rijeka – Urinj. Fund of Professional Documentation of the Faculty of Agronomy, Department of General Agronomy, Zagreb (in Croatian)
- Knežević K., Kruljac A., Bašić Končar M., Pišl Z., Lisjak D. Environmental Protection Report on the Need of Assessment for Remediation and Closure of Non-hazardous Waste Landfill Šoići within the Oil Refinery Rijeka. Kaina. d.o.o., Zagreb, 2017 (in Croatian)
- Korlević M., Zucko J., Najdek Dragić M., Blažina M., Pustijanac E., Vojvoda Zeljko T., Gacesa R., Baranasic D., Starcevic A., Diminic J., Long P.F., Cullum J., Hranueli D., Orlić S. (2015). Bacterial diversity of polluted surface sediments in the northern Adriatic Sea. *Systematic and Applied Microbiology* 38 (3): 189- 197. doi: 10.1016/j.syapm.2015.03.001.
- Linšak Z., Tomić Linšak D., Glad, M., Cenov A., Čoklo M., Čoklo M., Manestar D., Mićović V. (2012). Ecotoxicological Characterization of Marine Sediment in Kostrena Coastal Area. *Collegium antropologicum* 36 (4): 1401-1405
- LNG Hrvatska d.o.o. (2019). LNG terminal Krk – gas hub for Central and Southeastern Europe. Available at: <https://www.lng.hr/hr/> [Accessed June 6th, 2017] (in Croatian)
- Lovrić D., Antolović A., Šubašić D. (2004). Establishment and Proposal for Remediation of Contamination on the Site of the Former Coke Plant in Bakar. *Brownfield Sites II-Assessment, Rehabilitation and Development* (Donati A., Rossi C., eds) University of Siena, Italy and C.A. Brebbia, Wessex Institute of Technology, UK. doi:10.2495/BF040121
- Matković N., Alebić-Juretić A. (1998). Emissions and Ambient Levels of Sulphur Dioxide in the Rijeka by Area. *Archives of Industrial Hygiene and Toxicology* 49 (2): 155-163
- Matković V., Matković N., Kontošić I., Jonjić A., Matković V. (1998). The Effect of Air Pollution on Ventilatory Function in Nonsmoking women. *Archives of Industrial Hygiene and Toxicology* 49 (1): 19-25.
- Mićović V., Alebić-Juretić A., Matković N., Crvelin G. Dustfall Measurements in Primorsko-Goranska County, 1975-2008 (2010). *Archives of Industrial Hygiene and Toxicology* 61 (1): 37-43. doi:10.2478/10004-1254-61-2010-1952
- Miko S., Durn G., Prohić E. (1999a). Evaluation of terra rossa geochemical baselines from Croatian karst regions. *Journal of Geochemical Exploration* 66 (1-2): 173-182
- Miko S., Mesić S., Hasan O., Šparica Miko M. (2010). Investigation of heavy metals and organic compounds in sediments of watersheds in Istria and north Dalmatia, a study. *Archives of the Croatian Geology Institute* (in Croatian)
- Miko S., Peh Z., Bukovec D., Kastmüller Ž., Antonić O. (1999b). Topsoil geochemistry as a consequence of acid rain deposition at an abrupt climate boundary, the case of National Park "Risnjak", Croatia. In: 19th International Geochemical Exploration Symposium, Exploration Geochemistry into the 21st Century; Symposium Program and Abstracts Volume (Fletcher W. K., Elliot, I. L., eds). Vancouver: AEG, GSI.
- Miko S., Peh Z., Bukovec D., Prohić E., Kastmüller Ž. (2000). Geochemical Baseline Mapping and Lead Pollution Assessment of Soils on the Karst in Western Croatia. *Natura Croatica: Periodicum Musei Historiae Naturalis Croatici* 9 (1): 41-59
- Narodne novine (2019). Regulation on the Protection of the Agricultural Land from Pollution. *Narodne novine* d.d. 71/2019, Zagreb, Croatia (in Croatian)
- Ozretić B., Krajnović-Ozretić M., Santin J. (1990). As, Cd, Pb, and Hg in benthic animals from the Kvarner-Rijeka Bay region, Yugoslavia. *Marine Pollution Bulletin* 21(12): 595-598
- Pajić D., Glavan M. – The fifth wheel – INA doesn't know what to do with Mlaka refinery. *Novi List* [online] 2011. Available at: http://www.novolist.hr/Vijesti/Rijeka/Zadnja-rupa-na-svirali-Ina-ne-zna-sto-bi-s-rafinerijom-na-Mlaki?meta_refresh=true [Accessed June 6th, 2017] (in Croatian)
- Pandey, J. S., Kumar, R., & Devotta, S. (2005). Health risks of NO₂, SPM and SO₂ in Delhi (India). *Atmospheric Environment*, 39(36): 6868-6874
- Paparella S. Dina Petrochemicals declared blackspot, remediation pending. *Poslovni dnevnik* [online] 2017. Available at: <http://www.poslovni.hr/hrvatska/postrojenju-dine-prvo-etiketa-crne-tocke-pa-sanacija-326589> [Accessed June 6th, 2017] (in Croatian)
- Perić L., Fafanđel M., Glad M., Bihari N. (2012a). Heavy metals concentration and metallothionein content in resident and caged mussels *Mytilus galloprovincialis* from Rijeka bay, Croatia. *Fresenius environmental bulletin* 21 (9): 2785-2794
- Perić L., Smodlaka Tanković M., Ravlić S. (2012b). Evaluation of marine water quality along North-Eastern Adriatic coast based on lysosomal membrane stability in mussels *Mytilus galloprovincialis* Lam. - A long term study. *Acta Adriatica: international journal of Marine Sciences* 53 (3): 457-465
- Petrak A. Municipality of Viškovo requested suspension of procedure for issuing site permit for remediation of "black pit" Sovjak. *Novi List* [online] 2016. Available at: <http://www.novolist.hr/Vijesti/Rijeka/Opcina-Viskovo-zatrazila-obustavu-postupka-izdavanja-lokacijske-dozvole-za-sanaciju-crne-jame-Sovjak> [Accessed June 7th, 2017] (in Croatian)
- Picer M. (1991). Levels and long-term trends of some high molecular chlorinated hydrocarbons in mussels collected from the western Istrian coastal waters — northern Adriatic. *Chemosphere* 23 (6): 747-759
- Picer M. (2000). DDTs and PCBs in the Adriatic Sea. *Croatica Chemica Acta* 73 (1): 123-186
- Picer M., Picer N., Ahel M. (1978). Chlorinated insecticide and PCB residues in fish and mussels of east coastal waters of the middle and north Adriatic Sea, 1974-75. *Pesticides Monitoring Journal* 12 (3): 102-112
- Picer N. (1990). Chlorinated Insecticides and Polychlorinated Biphenyls in the Rijeka Bay Aquatorium. Dissertation, University of Zagreb.
- Picer N., Picer M. (1992). Inflow, levels and the fate of some persistent chlorinated hydrocarbons in the Rijeka Bay area of the Adriatic Sea. *Water Research* 26 (7): 899-909
- Picer N., Picer M. (1986). Chlorinated insecticides and PCBs in asteroidea and holothuroidea species from Rijeka Bay, Yugoslavia. *Science of the Total Environment* 57 (1): 39-47
- Popadić A., Vidović J., Čosović V., Medaković D., Dolenc M., Felja I. (2013). Impact evaluation of the industrial activities in the Bay of Bakar (Adriatic Sea, Croatia): recent benthic foraminifera and heavy metals. *Marine Pollution Bulletin* 76 (1-2): 333-348

- Poslovni dnevnik (2015). Supervision over Dina Petrochemicals to be taken over by the state. Available at: <http://www.poslovni.hr/domace-kompanije/nadzor-nad-dinom-petrokemijom-od-1-studenoga-preuzima-drzava-303894> [Accessed June 7th, 2017] (in Croatian)
- Poslovni dnevnik (2016). Dina's Chlorine taken to Kutina Petrochemicals [online]. Available at: <http://www.poslovni.hr/hrvatska/klor-iz-dine-odvezen-u-petrokemiju-311579> [Accessed June 7th, 2017] (in Croatian)
- Prohić E., Hausberger G. and Davis, J. C. (1997). Geochemical patterns in soils of the Karst region, Croatia. *Journal of Geochemical Exploration* 60 (2): 139-155
- Prtenjak M. T., Jeričević A., Kraljević L., Bulić I. H., Nitis T. and Klaić, Z. B. (2009). Exploring atmospheric boundary layer characteristics in a severe SO₂ episode in the north-eastern Adriatic Atmospheric Chemistry and Physics 9: 4467–4483
- Ribić I. (2008). Sustainable redevelopment of hazardous waste landfills – the hazardous waste landfill of Sovjak (Rijeka, Croatia) as case study. *Natura Croatica : Periodicum Musei Historiae Naturalis Croatici* 17 (4): 375-384
- Rožmarić M., Rogić M., Benedik Lj., Štrok M., Barišić D., Gojmerac Ivšić A. (2012). ²¹⁰Po and ²¹⁰Pb activity concentrations in *Mytilus galloprovincialis* from Croatian Adriatic coast with the related dose assessment to the coastal population. *Chemosphere* 87 (11): 1295-1300
- Šinik N., Lončar E., Marki A. (1994). SO₂ Background Air Pollution in the Bakar Bay. *Croatian meteorological Journal* 29 (29): 21-24
- Tomić Linšak D., Linšak Ž., Bešić D., Vojčić N., Teležar M., Čoklo M., Susnić S., Mićović V. (2011). Polycyclic aromatic hydrocarbons and heavy metals in Kostrena coastal area. *Collegium antropologicum* 35 (4): 1193–1196
- Traven L. (2015). Sources, trends and ecotoxicological risks of PAH pollution in surface sediments from the northern Adriatic Sea (Croatia). *Marine Pollution Bulletin* 77(1): 445-450
- Traven L., Furlan N., Cenov A. (2015). Historical trends (1998–2012) of nickel (Ni), copper (Cu) and chromium (Cr) concentrations in marine sediments at four locations in the Northern Adriatic Sea. *Marine Pollution Bulletin* 98 (1-2): 289-294
- Valerjev Ogurlić N. A new life for the industrial complex in the centre of Rijeka: Refinery Mlaka to become a science and technology park. *Novi List* [online] 2016. Available at: <http://www.novolist.hr/Vijesti/Rijeka/Novi-zivot-industrijskog-kompleksa-u-centru-Rijeke-Rafinerija-na-Mlaki-postaje-znanstveno-tehnoloski-park> [Accessed June 6th, 2017] (in Croatian)
- Vrbek B., Buzjak N. (2004). Contribution to the knowledge of the content of heavy metals (Pb, Cu, Zn) in speleological objects in the Risnjak National Park (Croatia). *Acta carsologica* 33 (2): 181-188
- Vrbek B., Gašparac M. (1992). New imission findings of heavy metals in the National Park "Risnjak". *Radovi*. 27 (1): 65-75 (in Croatian)
- Vrbek B., Vrbek M., Vukelić J. (1991). Soil Acidification and Accumulation of Pb, Cu, Zn in Fir Forest Communities of National Park "Risnjak" ". *Forestry review* 115 (3-5): 163-172 (in Croatian)
- Zubak, V. Mifka, B., Alebić-Juretić, A. (2017). Temporal trends of airborne ozone concentrations in the Rijeka Bay area, Croatia– new regulation required? Abstracts of the 10th Croatian scientific and professional assembly Air Protection '17. October 03-07th, Primošten, Croatia.