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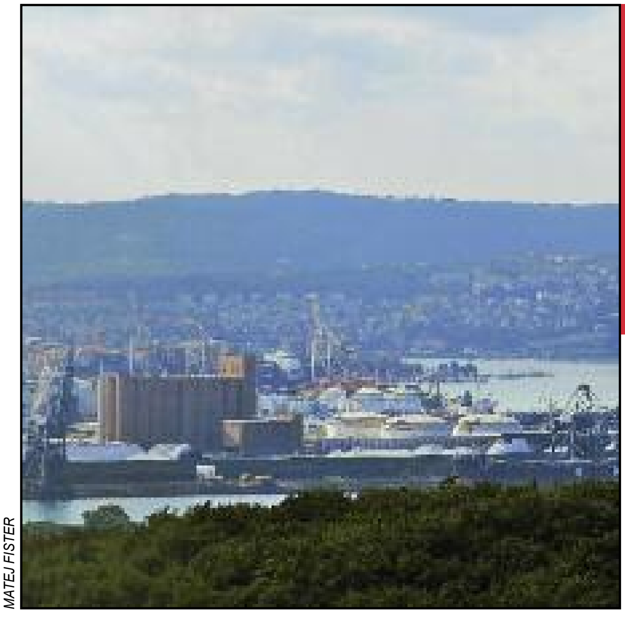
ENVIRONMENTAL IMPACT OF DUSTING FROM THE KOPER PORT BULK CARGO TERMINAL ON THE AGRICULTURAL SOILS

OKOLJSKI VPLIV PRAŠENJA S TERMINALA KOPRSKEGA PRISTANIŠČA ZA RAZSUTI TOVOR NA KMETIJSKA TLA

Nina Zupančič, Aleksander Horvat, Simona Skobe


MATEJ FISTER

Bulk cargo terminal of Luka Koper port could threat the environmental pollution
in the case of accidental dusting of potentially toxic material.
Terminal za razsuti tovor Luke Koper lahko v primeru nehotenega prašenja
onesnaži okolje s potencialno strupenimi snovmi.

Environmental impact of dusting from the Koper port bulk cargo terminal on the agricultural soils

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ABSTRACT: Areas around seaports are prone to environmental damage. In the port of Koper, Slovenia hematite was transhipped during a strong wind. The broader area was accidentally covered with hematite dust. Since the soils had already been geochemically mapped, we repeated the sampling to compare the geochemical composition of the topsoil. No soil contamination was established. The enrichment factors show depletion of majority of elements. According to the distances from the dust source, SiO_2, Na_2O and Cr have decreasing, and Fe_2O_3 increasing trends. The SiO_2 and Cr content correspond to the concentration of quartz rich sand, and the dissolution of carbonate closer to the sea. Co and Ni are probably bound to the clay minerals. Cu, Pb, and Zn could have some anthropogenic contribution.

KEY WORDS: soil contamination, micaceous hematite, dusting, seaport, Northern Adriatic Sea, Port of Koper, Slovenia

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ADRESSES:
Nina Zupančič, Ph.D.
University of Ljubljana, Faculty of natural sciences and engineering, Department of geology
Aškerčeva cesta 12, SI – 1000 Ljubljana, Slovenia
and
Ivan Rakovec Institute of paleontology
Research Center of the Slovenian Academy of Sciences and Arts
Novi trg 2, SI – 1000 Ljubljana, Slovenia
E-mail: nina.zupancic@ntf.uni-lj.si

Aleksander Horvat, Ph.D.
Ivan Rakovec Institute of paleontology
Research Center of the Slovenian Academy of Sciences and Arts
Novi trg 2, SI – 1000 Ljubljana, Slovenia
E-mail: ahorvat@zrc-sazu.si

Simona Skobe, Ph.D.
University of Ljubljana, Faculty of natural sciences and engineering, Department of geology
Aškerčeva cesta 12, SI – 1000 Ljubljana, Slovenia
E-mail: simona.skobe@ntf.uni-lj.si

1 Introduction

Seaports are major hubs of economic activity and of environmental pollution in coastal urban areas (Bailey and Solomon 2004). Activities at seaports can seriously affect local communities and marine- and land-based ecosystems throughout a region. These impacts range from increased cancer risk to the contamination of water bodies and soil (Bailey and Solomon 2004).

The main air pollutants related to port activities include diesel exhaust, particulate matter (PM), volatile organic compounds (VOCs), nitrogen oxides (NOx), ozone, and sulphur oxides (SOx). Other air pollutants from port operations such as carbon monoxide (CO), formaldehyde, heavy metals, dioxins and pesticides used to fumigate produce can also be a problem (Bagley et al. 1996; Bailey and Solomon 2004; Sharma 2006). Most articles dealing with seaport pollution concentrate on ship exhaust (Saxe and Larsen 2004; Tzannatos 2010) and the contamination of marine sediments and biota (Solis-Weiss et al. 2004; Adamo et al. 2005; Cukrov et al. 2011).

Less is known about the effects of dusting at bulk cargo terminals on soil. During cargo handling operations, emissions can often occur. The dust is often primary of concern due to its highly visible nature. If cargoes include harmful substances, accidents involving them may affect the environment. The severity of pollution will depend on the nature of the substance and the amount and concentration released into the port environment (Internet 1).

Northern Adriatic coast region has been populated since Roman times and settlements have depended on agriculture, viticulture, fishing and trade. Still now, the area produces significant share of vegetables and grapes. With the development of the ports new source of pollution has emerged, possibly influencing the content of heavy metals in soil. In different regions of Slovenia and abroad several authors studied soil contamination from different point of view (i.e. Aubert and Pinta 1977; Kabata–Pendias and Pendias 1984; Alloway 1990; Adriano 2001; Zupan, Grčman and Lobnik 2008; Andjelov 2012) but none of the studies focused on seaport as possible source of potentially toxic elements.

Situated in the Slovenian part of the northern Adriatic Sea, the Port of Koper (Luka Koper) is a multi-purpose port that has the status of an entry point for goods designated for the European Union. The port's Terminal for Minerals handles minerals, industrial minerals and other bulk material, mostly bauxite, borax, cement, phosphates, ilmenite, clinker, perlite, sintermagnesite, scrap etc. (Internet 2).

The port operations create emissions of different materials into the atmosphere. Airborne dust levels increase during the handling of particulate bulk cargos. Special measures during dry windy weather are taken (Internet 3).

In spite of them, accidental dusting occurred in March 2011 due to a very strong bora wind blowing 7.3 m/s during the transhipment of bulk cargo. Institute of Public Health Maribor estimated that in four days 1000 kg of dust was emitted (Žerjal 2011). Iron oxide dust covered the town of Koper and surrounding area. The company published the material safety data sheet provided by the owner of the goods, which was in line with international standards. According to it, the material was MIOX®, physiologically harmless natural micaceous hematite (α-Fe_2O_3), used for applications in anticorrosive and decorative paints, plastics, rubber and ceramic industries (Internet 4). However, some members of the public claimed the dust was toxic, as unofficial results of the analyses had shown that the dust contained not only particles of iron oxide, but also magnesium, aluminium, cobalt and nickel (Internet 5).

In 2008 a study was performed to evaluate the influence of four main possible contamination sources in the area – the port, viticulture, a chemical factory and agriculture (Zupančič and Skobe 2014). The results of this study served as background values of soil heavy metal content.

In present study, the influence of the 2011 dusting on the geochemical composition and contamination of the soils is estimated.

2 Materials and methods

The broader area topography is characterised by hilly hinterland developed on Eocene carbonate flysch rocks, and the Holocene alluvial plains of the Rižana and Badaševica rivers (Pleničar et al. 1973). The soil's parent material is derived from weathered flysch and the soil types are eutric (TIS/ICPVO 1990–2015).

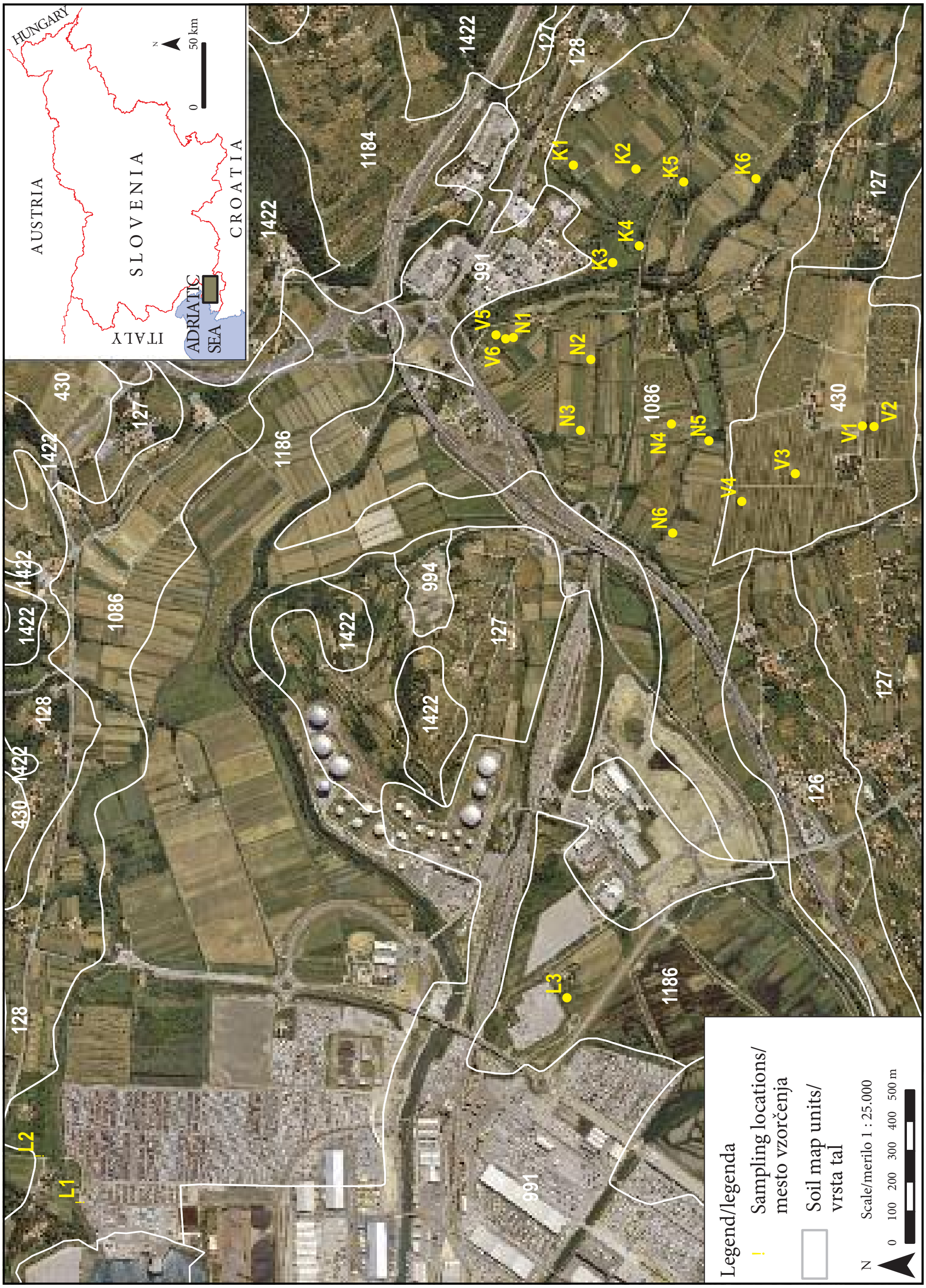

Figure 1: Soil sampling locations in the Koper area. Legend: 430 – deep cultivated (trench – ploughed) soil, eutric, 100 %; 1086 – alluvial soils, eutric, deep, on loamy alluvium, 60 % and alluvial soils, eutric, deeply gleyed, on loamy alluvium, 40 %; 1186 – gley, eutric, mineral, medium strong, 50 % and gley, eutric, mineral, moderately strong, 50 % (soil map after TIS/ICPVO 1990–2015).

In 2011 after the accidental dusting soil was sampled from the same locations as in 2008 study (Figure 1), although three locations around the port were unfortunately no longer reachable due to construction works. In 2008 study (Zupančič and Skobe 2014) sampling locations were chosen according to land use (agriculture (N1 – N6), viniculture (V1 – V6), vicinity of port (L1 – L3) and chemical factory (K1 – K6)). Micro locations were selected according to the concept of random sampling (Davis 1986). 21 topsoil (15 cm) samples weighing 1.5–2 kg were collected. According to the soil map (TIS/ICPVO 1990–2015) the port samples soil type was gley (Eutric Gleysol (IUSS 2014)) developed on natural and partly artificially filled in marine and river sediments of a local flysch origin. The vineyard samples from locations owned by the wine producing company (V1 – V4) were on slopes, with the soil type being deep cultivated (trench – ploughed) soil (Eutric Cambisol (Aric) (IUSS 2014)), developed on Eocene flysch. Soils from two private vineyards (V5, V6), the vicinity of industrial factory, and farmland are alluvial, developed on flysch alluvium (Eutric Fluvisol (IUSS 2014)).

The soil samples were air-dried, ground, split and sieved to < 0.063 mm to produce a 20 g sample. ACME Analytical Laboratories in Canada determined their chemical composition. Total abundances of the major oxides and several minor elements were reported on a 0.2g sample analysed by ICP-emission spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) is by weight difference after ignition at 1000 °C. Total carbon (TOT/C) and sulphur were determined by the Leco method. Refractory elements were determined by ICP mass spectrometry following same decomposition. In addition a separate 0.5g split was digested in Aqua Regia and analysed by ICP Mass Spectrometry to report the precious and base metals. The accuracy, precision and detection limits were established as good for the majority of elements, except Ag, Au, As, Be, Cd, Hg, Mo, Se, Sb, Sn, Tl and W, which were excluded from further discussion.

The normality of the distribution of the data was tested visually from histogram and normal probability plots, with comparisons of the mean, geometric mean and median, the testing of skewness and kurtosis, and Shapiro-Wilk's test, as proposed by Madansky (1988). The data were transformed to a more symmetric distribution with a Box-Cox transformation (Box and Cox 1964). Statistical tests were computed with transformed data for all variables but the descriptive statistics and graphical illustrations with the raw data are presented.

3 Results and discussion

Descriptive statistics for each element in each year are summarised in Table 1.

The dusting event should have resulted in elevated concentrations of elements claimed as toxic, i.e. besides Fe also Mg, Al, Co and Ni. A statistical t-test comparison of the soil geochemistry from both years did not confirm any differences in any elemental concentrations, with the exception of Co, for which even an on average 2 mg/kg lower content was established in 2011. The dusting seems not to influence the chemical composition of the topsoil. For Al_2O_3, MgO and Cr the mean values are similar in both years, but their variability is even less in 2011. After the dusting, the Fe_2O_3, Co, Cu, Pb and Zn mean values decreased, but the variability remained similar.

With respect to the situation before dusting all heavy metals, except Cr, and some major elements, including Fe_2O_3, exhibited somewhat lower mean values (Table 1). Regarding the median values, the differences between both sampling years are even less pronounced as median values are not prone to extreme values i.e. contamination.

Low coefficients of variation (CV) point to natural and high CVs to human-introduced sources of variability. For the majority of elements the CVs dropped between the two sampling years, but even the increased CV values are still only around 10 for Co and Cr, around 20 for Ni and Zn and around 30 for Cu and Pb, which could be interpreted as a natural background with some possible anthropogenic influence.

Although there are no differences between elemental contents of soils sampled in before and after accidental micaceous hematite dusting, they may exist between the sample locations at different distances from the dust source. We divide the area into three zones: < 1.5 km (L2, L3), 3–3.5 km (N1 – N6 and V3 – V6) and 3.5–4 km (K1 – K6 and V1 – V2) distance from the bulk cargo terminal. Analyses of variance showed 95% probable differences in the contents of SiO_2, Na_2O, MnO, LOI, C/TOT and Cr according to their distance from the port.

Figure 2 shows decreasing trends from the port to the inland for SiO_2, Na_2O and Cr and somewhat less persuasive trends for Pb and Zn. For SiO_2, Na_2O and Cr the reason could be their concentration in the sand fraction of alluvium (Zupančič and Skobe 2014). Pb and Zn distribution is masked by rather high variation, probably due to the natural variability of soils, sampling/analytical error or some other reason. Still, the higher values near the port could be attributed to pollution due to exhaust from vehicles, ships and different engines used in port (Fröhling and Ludzay 2002; Kummer et al. 2009). For Cu and Ni the trends are kinked – somewhat lower close to the port than in the 3–3.5 km zone and again dropping in the most distant zone. In the case of Cu, it possibly reflects the somewhat elevated Cu content in vineyards (Baker and Senft 1995; Besnard et al. 2001; Rusjan et al. 2006). For Ni, the reason could be the high natural variability.

Table 1: Descriptive statistics of major elements (%) and heavy metals (mg/kg) for 2008 (the first row), and 2011 (the second row). LOI – loss on ignition, TOT/C – total carbon.

	Mean	Geometric mean	Median	Minimum	Maximum	Standard deviation	Coefficient of variation
SiO_2	53.0	52.8	51.9	44.7	63.2	4.68	8.8
	52.8	52.7	51.4	45.7	64.5	4.59	8.7
Al_2O_3	10.0	9.9	10.0	8.4	11.8	0.99	10.0
	10.1	10.1	10.2	9.0	11.4	0.82	8.1
Fe_2O_3	4.4	4.4	4.3	3.7	5.1	0.40	9.1
	4.3	4.3	4.3	3.8	4.9	0.33	7.8
MgO	1.4	1.4	1.4	1.0	2.8	0.35	24.6
	1.4	1.4	1.4	1.2	1.6	0.11	8.3
CaO	10.7	10.3	11.1	4.1	14.2	2.66	24.9
	10.9	10.6	11.8	4.6	14.0	2.40	22.0
Na_2O	0.9	0.9	0.9	0.7	1.1	0.08	8.2
	1.0	1.0	1.0	0.8	1.1	0.081	8.2
K_2O	1.607	1.7	1.7	1.4	2.1	0.16	9.6
	1.7	1.7	1.8	1.5	2.1	0.16	8.9
TiO_2	0.6	0.6	0.6	0.5	0.7	0.05	8.9
	0.6	0.6	0.6	0.5	0.7	0.04	7.1
P_2O_5	0.17	0.17	0.17	0.13	0.25	0.04	21.1
	0.17	0.17	0.18	0.08	0.24	0.04	23.6
MnO	0.11	0.10	0.11	0.05	0.13	0.017	15.7
	0.11	0.10	0.11	0.06	0.13	0.02	20.8
LOI	16.8	16.6	17.5	11.8	20.5	2.58	15.3
	16.7	16.6	17.2	10.8	20.2	2.20	13.2
C/TOT	4.0	3.8	4.0	1.8	5.7	0.99	24.9
	3.9	3.8	4.0	1.7	4.9	0.77	19.7
Co	18.1	18.0	18.1	14.3	20.9	1.63	9.0
	16.6	16.6	17.0	13.5	18.7	1.56	9.4
Cr	216.6	214.7	212.3	178.1	315.1	30.28	14.0
	221.1	219.6	219.2	184.9	294.5	27.49	12.4
Cu	51.5	46.8	44.9	31.8	180.90	31.66	61.4
	44.4	42.9	40.1	29.8	77.8	12.73	28.7
Ni	80.3	80.0	80.2	64.0	91.8	6.40	8.0
	78.9	76.4	82.5	47.8	95.0	14.65	18.8
Pb	18.6	18.2	17.4	13.4	30.3	4.14	22.2
	16.5	15.6	17.6	7.0	26.2	4.82	29.2
Zn	71.5	67.9	64.0	57.0	212.0	32.91	46.0
	66.7	65.1	67.0	40.0	105.0	14.57	21.8

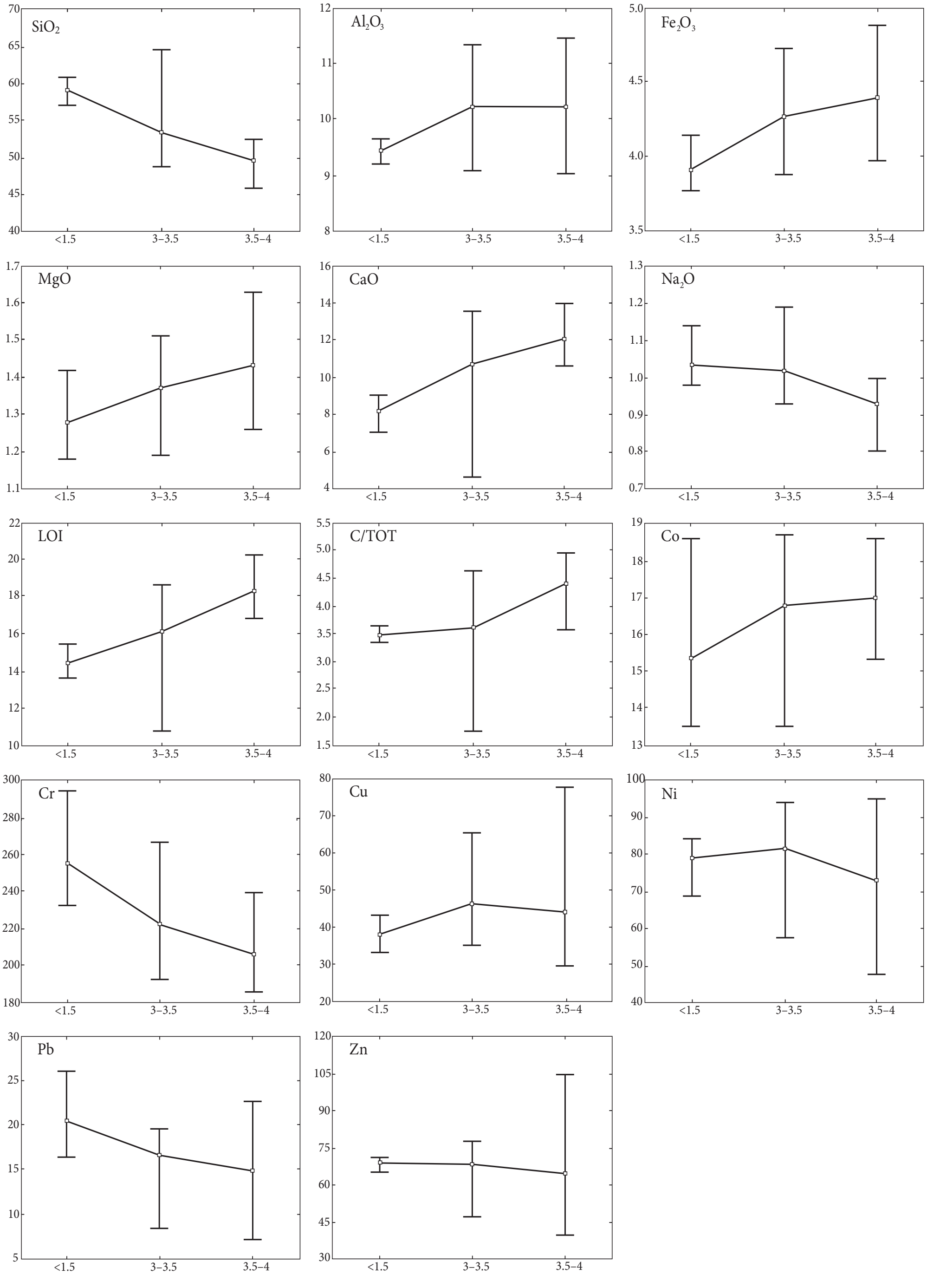

Figure 2: Mean (point) and range (minimum – maximum) values of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, CaO, Na$_2$O, LOI, C/TOT (all in %), Co, Cr, Cu, Ni, Pb and Zn (all in mg/kg) in 2011 in three different distance zones (in km) from the port.

Because of the mineral composition of soils (Zupančič and Skobe 2014), which reflects quartz richer sand vs. carbonate richer clay fraction, the trends of Al_2O_3, MgO, CaO, LOI and C/TOT are increasing in the inland direction (Figure 1). The Al_2O_3 variability and mean value are lowest closest to the port so the dusting event as a reason for its content is excluded. Co has the same trend, but in all three zones a very wide range of values. Moreover, the Fe_2O_3 trend is increasing from the port to the hinterland, not proving the influence of the hematite deposition.

Enrichment factors (EF) of »critical« elements (Al_2O_3, Fe_2O_3, MgO, Co, Cr, Cu, Ni, Pb, Zn), calculated as the ratio between the concentrations observed after the dusting in 2011 and before it in 2008 (Manta et al. 2002; Acosta et al. 2009), are presented in Table 2. If EF is greater than one, the concentration of the metal is higher than the local background value, which may be an indication of the influence of anthropogenic inputs on the soils (Luo et al. 2012). An obvious feature is that these elements do not follow the same pattern in different locations. Generally, the depletions are higher than the enrichments and the EFs are so low that they can be attributed to natural or analytical variability and not pollution due to the dusting.

Hematite is mined in the Waldenstein mine in Austria (Internet 3). Vein-type mineralisation is situated in metamorphosed schists of the Koralm Crystalline Complex. Hematite contains > 92% Fe_2O_3, up to 6% TiO_2 and a minor content of MnO and V_2O_3. In chlorite-hematite ore there could be around 6% Al_2O_3, 3.5% MgO, and 4 mg/kg Ni (Prochaska et al. 1995). It is thus not very surprising that some country rock particles in the ore could contribute to the elevated Al_2O_3 and MgO reported in the media as being »dangerous«. Hematite itself is quite inert. Ni and Co could also be present in minor amounts in original ore, substituting for Fe in hematite crystal lattice. In that form, they are also harmless to humans.

Table 2: Enrichment factors for all locations arranged in increasing distance from the port for selected elements. Enriched values are shown in bold.

	Al_2O_3	Fe_2O_3	MgO	Co	Cr	Cu	Ni	Pb	Zn
L1	0.98	0.88	0.44	0.85	**1.21**	0.21	**1.06**	0.62	0.33
L2	**1.10**	**1.11**	**1.15**	**1.14**	1.00	0.77	**1.12**	0.97	**1.07**
L3	**1.03**	0.98	**1.03**	0.97	0.93	0.59	**1.08**	**1.06**	**1.09**
N6	0.96	0.93	**1.13**	0.88	0.83	**1.16**	**1.12**	0.87	**1.26**
V4	**1.02**	0.91	**1.08**	0.76	0.97	**1.40**	**1.16**	**1.12**	**1.23**
N3	**1.04**	**1.02**	**1.02**	**1.04**	**1.07**	**1.17**	**1.05**	**1.07**	**1.10**
N5	0.98	0.93	0.88	0.93	**1.03**	**1.04**	0.93	0.82	**1.02**
V5	**1.05**	0.97	**1.05**	0.92	**1.10**	**1.18**	**1.03**	**1.04**	**1.11**
V6	**1.08**	**1.01**	**1.08**	**1.03**	1.00	0.63	**1.06**	0.80	1.00
N1	0.98	0.91	0.95	0.94	**1.15**	0.91	0.97	0.96	**1.02**
N4	**1.01**	0.98	**1.01**	0.92	1.00	0.77	0.67	0.37	0.62
N2	**1.10**	**1.07**	**1.11**	**1.02**	**1.06**	**1.04**	**1.17**	**1.15**	**1.16**
V3	0.98	0.92	0.98	0.79	**1.08**	**1.09**	**1.02**	**1.12**	**1.11**
V1	**1.02**	0.95	**1.09**	0.79	0.94	**1.36**	**1.05**	**1.08**	**1.16**
V2	**1.05**	0.97	**1.03**	0.91	**1.15**	0.59	0.58	0.52	0.63
K3	0.98	1.00	0.97	0.90	**1.07**	**1.09**	**1.08**	**1.13**	**1.10**
K4	0.95	0.92	1.00	0.88	0.94	**1.02**	0.53	0.67	0.67
K2	0.98	0.95	0.94	0.73	1.00	**1.17**	**1.03**	**1.02**	**1.19**
K1	**1.08**	0.97	**1.08**	0.95	**1.03**	**1.27**	**1.09**	**1.14**	**1.14**
K5	0.97	0.94	0.94	**1.02**	**1.04**	1.00	0.99	0.98	**1.23**
K6	**1.06**	**1.03**	**1.02**	**1.05**	0.97	**1.08**	0.70	0.39	0.79

Combining the data for the two years (location L1 is excluded as 2008 established contamination was obviously sanitized) enables multivariate statistics approach (Swan and Sandilands 1995). Extracting three factors based on principle component analysis explains nearly 70% of all observed variations. Unrotated factor loadings reflect geological vs. anthropogenic influences. The first factor comprises high SiO_2, Na_2O and Cr reflecting high quartz, i.e. sand fraction content closer to the sea. Accordingly, this factor has high negative CaO, LOI, C/TOT loadings due to low calcite amount. The second factor expresses clay minerals content (high positive Al_2O_3, Fe_2O_3, MgO, K_2O, TiO_2). It seems that Co and Ni could at least partly be bound to these minerals. The third factor gathers heavy metals Cu, Ni, Pb and Zn, with Co, P_2O_5 and MnO having negative loadings. The mentioned groups of minerals/elements are presented in Figure 3. Probably anthropogenic Zn and Pb could be a consequence of motor vehicle traffic as some Pb is found in unleaded and diesel fuels (Fröhling and Ludzay 2002; Kummer et al. 2009), and Zn is a component of rubber tyres (US EPA 1979). Cu could have a double source – the use of fungicides in vineyards (Besnard et al. 2001; Rusjan et al. 2006) and as well traffic (Cadle et al. 1997). The high Ni content could be natural (Zupančič and Skobe 2014) or at least partly a consequence of the combustion of fuel in stationary sources (Pacyna et al. 2007).

4 Conclusion

Soils developed on the alluvium of carbonate flysch rocks sampled in 2008 enabled the estimation of the possible heavy metals content increase due to accidental dusting, emitting 1000 kg of material in 2011 when hematite was being transhipped during very strong winds (7.3 m/s) in the Luka Koper. Unofficial results of the chemical analysis of the dust had shown that besides the iron there was some Al, Mg, Co and Ni. Some members of the public claimed that the dust had polluted the environment and was harmful to the population.

According to our research, the sequence of the content of elements is the same in both sampled datasets, and is typical for soils developed on flysch rocks rich in Cr and Ni.

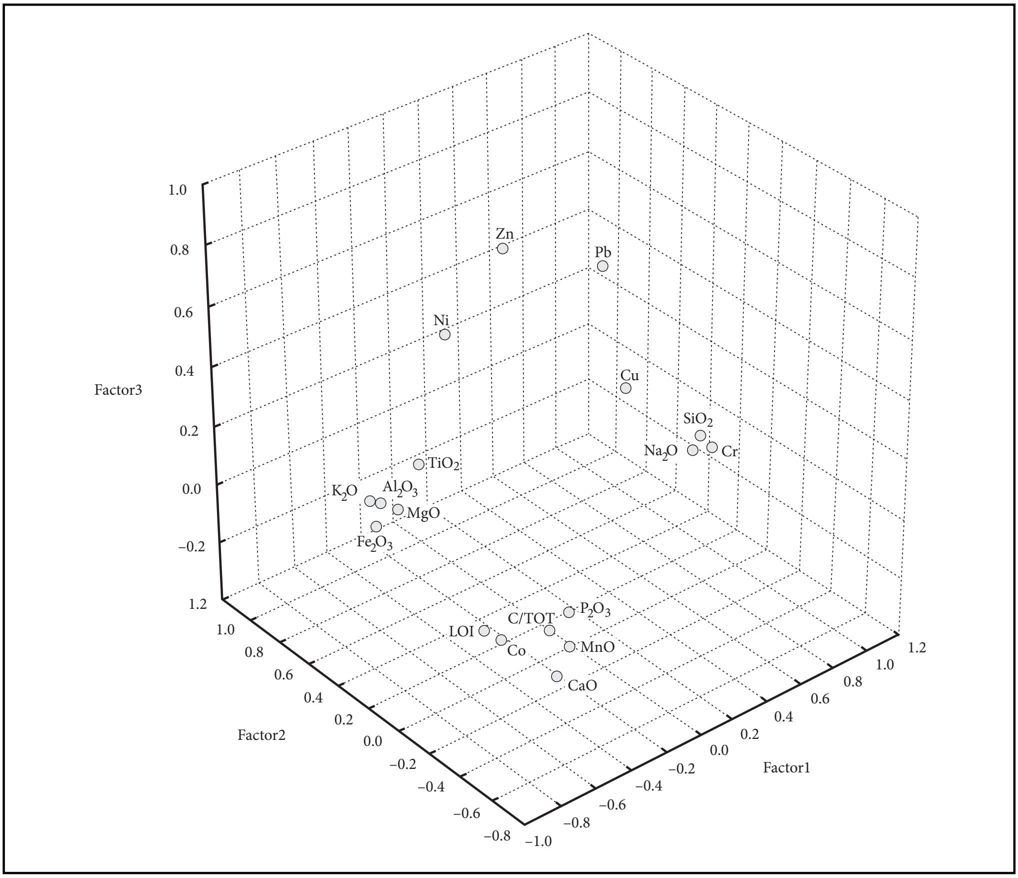

Figure 3: Factor loadings for the major elements and heavy metals of soils from the port hinterland sampled in 2008 and 2011. Location L1 is excluded.

The only element, which shows a statistically different content between the two years, is Co, although its values are even a little lower after dusting than before it. The established mean values of Al_2O_3, MgO and Cr remained similar, and the Fe_2O_3, Co, Cu, Ni, Pb and Zn mean values are lower in 2011. Regarding the median values, the differences between both sampling years are even less pronounced. For the majority of elements (Al_2O_3, Fe_2O_3, K_2O, CaO, MgO, TiO_2, LOI, C/TOT, Cr, Cu, Zn) the CVs dropped between the two sampling years, but for some of them they actually increased (P_2O_5, MnO, Co, Ni, Pb). However, the CV values are still only around 10 for Co and Cr, around 20 for Ni and Zn and around 30 for Cu and Pb, which points to a major geogenic and minor anthropogenic source of heavy metals.

A comparison of three zones at < 1.5 km, 3–3.5 km, and 3.5–4 km distance from the bulk cargo terminal showed differences in contents of SiO_2, Na_2O, MnO, LOI, C/TOT and Cr. The mean values of SiO_2, Na_2O, Cr, Pb and Zn decrease with increasing distance from the port. For SiO_2, Na_2O and Cr the reason could be their concentration in the sand fraction of alluvium and later in the soils developed on it. For Cu and Ni, the values are lower close to the port, higher in the 3–3.5 km zone and again lower in the most distant zone. The Cu distribution possibly reflects the use of fungicides in vineyards. Reasons for the Ni, Pb and Zn variability could be natural, analytical or human. Al_2O_3, MgO, CaO, LOI and C/TOT are increasing in the inland, reflecting more carbonate and clay with respect to quartz. Co follows the same trend, but its variability is huge. The Fe_2O_3 trend is increasing from the port to the hinterland, not proving the influence of the hematite deposition.

Enrichment factors calculated for two sampling locations nearest to the port (L2, L3) indicate that Al_2O_3, MgO, Ni and Zn are slightly enriched, F_2O_3 and Co are enriched in closest location (L2) and depleted in more distant one (L3), and Pb is enriched in L3 and depleted in L2. Cu is depleted and Cr nearly the same with respect to the situation before the dusting. However, where enrichments do exist the enrichment factors are so small that they are more likely natural or analytical variability and not due to the pollution with hematite.

Iron oxide is a natural material – hematite mined in metamorphic rocks. It is thus completely normal that a chemical analysis of dust also detected some Al_2O_3 and MgO, from the country rock. Ni and Co could be present in minor amounts in original ore, substituting for Fe in hematite crystal lattice. In that form, they are harmless to humans.

The factor analysis of the compiled data for both years clearly shows the influence of the parent material and possible contamination. The first factor is interpreted as the »distance from the sea« comprising a high level of SiO_2, Na_2O and Cr closer to the sea due to concentration of quartz and sand, and the dissolution of carbonate (CaO, LOI, C/TOT).The second factor expresses »clay content« with loadings of Al_2O_3, Fe_2O_3, MgO, K_2O and TiO_2. It seems that Co and Ni could be at least partly bound to these minerals as well. The third factor is named »heavy metals« as Cu, Ni, Pb and Zn are positively and Co, P_2O_5 and MnO negatively loaded. The anthropogenic Zn and Pb could be a consequence of motor vehicle traffic, and Cu could have a double source: the use of fungicides in vineyards and traffic. The Ni content could be natural or at least partly a consequence of the combustion of fuel.

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5 References

Acosta, J. A., Cano, A. F., Arocena, J. M., Debela, F., Martinez-Martinez, S. 2009: Distribution of metals in soil particle size fractions and its implication to risk assessment of playgrounds in Murcia City (Spain). Geoderma 149, 1-2. DOI: http://dx.doi.org/10.1016/j.geoderma.2008.11.034

Adamo, P., Arienzo, M., Imperato, M., Naimo, D., Nardi, G., Stanzione, D. 2005: Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. Chemosphere 61-6. DOI: http://dx.doi.org/10.1016/j.chemosphere.2005.04.001

Adriano, D. C. 2001: Trace elements in terrestrial enviornments. Biogeochemistry, bioavailability, and risk of metals. New York.

Alloway, B. J. 1990: Heavy metals in soils. Glasgow.

Andjelov, M. 2012: Regionalna porazdelitev geokemičnih prvin v tleh Slovenije. RMZ – Materials and geoenvironment 59, 2-3.

Aubert, H., Pinta, M. 1977: Trace elements in soils. Amsterdam.

Bagley, S. T., Baumgard, K. J., Gratz, L. D., Johnson, J. H., Leddy, D. G. 1996: Characterization of fuel and aftertreatment device effects of diesel emissions. Research report number 76. Michigan technological university, Department of biological sciences, Health effects institute. Houghton.

Bailey, D., Solomon, G. 2004: Pollution prevention at ports: clearing the air. Environmental impact assessment review **2**4, 7-8. DOI: http://dx.doi.org/10.1016/j.eiar.2004.06.005

Baker, D. E., Senft, J. P. 1995: Copper. Heavy Metals in Soil. New York.

Besnard, E., Chenu, C., Robert, M. 2001: Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils. Environmental pollution 112.

Box, G. E. P., Cox, D. R. 1964: An analysis of transformations. Journal of the royal statistical society B 26-2.

Cadle, S. H., Mulawa, P. H., Ball, J., Donase, C., Weibel, A., Sagebiel, J. C., Knapp, K. T., Snow, R. 1997: Particulate emission rates from in-use high-emitting vehicles recruited in Orange County, California. Environmental science & technology 31-12. DOI: http://dx.doi.org/10.1021/es9700257

Cukrov, N., Frančišković-Bilinski, S., Hlača, B., Barišić, D. 2011: A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia. Marine pollution bulletin 62-1. DOI: http://dx.doi.org/10.1016/j.marpolbul.2010.08.020

Davis, J. C. 1986: Statistic and data anlysis in geology. New York.

Fröhling, J. C., Ludzay, J. 2002: Composition of diesel fuels from German refineries. Hamburg.

Internet 1: http://www.ukmarinesac.org.uk/activities/ports/ph3_2.htm, 2001 (6. 9. 2012).

Internet 2: http://www.luka-kp.si/eng (6. 9. 2012).

Internet 3: http://www.zivetispristaniscem.si (6. 9. 2012).

Internet 4: www.kmi.at (6. 9. 2012).

Internet 5: http://www.delo.si/novice/slovenija/prasni-delci-iz-luke-niso-nedolzni.html/, 2011 (6. 9. 2012)

IUSS Working Group WRB 2014: World Reference Base for Soil Resources 2014.

International soil classification system for naming soils and creating legends for soil maps.

World soil resources reports 106. Rome.

Kabata-Pendias, A., Pendias, H. 1984: Trace elements in soils and plants. Boca Raton.

Kummer, U., Pacyna, J., Pacyna, E., Friedrich, R. 2009: Assessment of heavy metal releases from the use phase of road transport in Europe. Atmospheric environment 43-3. DOI: http://dx.doi.org/10.1016/j.atmosenv.2008.10.007

Luo, X., Yu, S., Zhu, Y., Li, X. 2012: Trace metal contamination in urban soils of China. Science of the total environment 421–422. DOI: http:/dx.doi.org/10.1016/j.scitotenv.2011.04.020

Madansky, A. 1988: Prescriptions for working statisticians. New York.

Manta, D. S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M. 2002: Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Science of the total environment 300-1-3. DOI: http://dx.doi.org/

Pacyna, E. G., Pacyna, J. M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., Nitter, S., Pregger, T., Pfeiffer, H., Friedrich, R. 2007: Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmospheric environment 41-38. DOI: http:/dx.doi.org/10.1016/j.atmosenv.2007.07.040

Pleničar, M., Polšak, A., Sikić, D. 1973: Osnovna geološka karta SFRJ 1 : 100.000, list Trst. Zvezni geološki zavod. Beograd.

Prochaska,W., Pohl, W., Belocky, R., Kucha, H. 1995: Tertiary metallogenesis in the Eastern Alps: the Waldenstein hematite deposit (Austria). Geologische Rundschau 84.

Rusjan, D., Strlič, M., Pucko, D., Šelih, V. S., Korošec-Koruza, Z. 2006: Vineyard soil characteristics related to content of transition metals in a sub-Mediterranean winegrowing region of Slovenia. Geoderma 136, 3-4. DOI: http:/dx.doi.org/10.1016/j.geoderma.2008.11.034

Saxe, H., Larsen, T. 2004: Air pollution from ships in three Danish ports. Atmospheric environment 38-24. DOI: http:/dx.doi.org/10.1016/j.atmosenv.2004.03.055

Sharma, D. S. 2006: Ports in a storm. Environmental health perspective 114-4. Bethesda.

Solis-Weiss, V., Aleffi, F., Bettoso, N., Rossin, P., Orel, G., Fonda-Umani, S. 2004: Effects of industrial and urban pollution on the benthic macrofauna in the Bay of Muggia (industrial port of Trieste, Italy). Science of the total environment 328, 1-3. DOI: http:/dx.doi.org/10.1016/j.scitotenv.2004.01.027

Swan, A. R. H., Sandilands, M. H. 1995: Introduction to geological data analysis. Oxford.

TIS/ICPVO 1990–2015: Talni informacijski sistem Infrastrukturnega centra za pedologijo in varstvo okolja, MRIC-UL, Biotehniška fakulteta. Ljubljana.

Tzannatos, E. 2010: Ship emissions and their externalities for the port of Piraeus Greece. Atmoshperic environment 44-3. DOI: http:/dx.doi.org/10.1016/j.atmosenv.2009.10.024

United States environmental protection agency (US EPA), Evaluation of particulate emission factors for vehicle tire wear. Research triangle park: Office of air quality planning and standards, EPA-450/4-79-014, 1979.

Zupan, M., Grčman, H., Lobnik, F. 2008: Raziskave onesnaženosti tal Slovenije. Elaborat, Agencija RS za okolje. Ljubljana.

Zupančič, N., Skobe, S. 2014: Antropogenic environmental impact in the Mediterranean coastal area of Koper/Capodistria, Slovenia. Journal of Soils and Sediments 14-1. DOI: http:/dx.doi.org/10.1007/s11368-013-0770-7.

Žerjal, E. 2011: Ocena tveganja za zdravje ljudi in ocena tveganja za okolje v primeru raztrosa sljudastega železovega oksida v Luki Koper. Elaborat, Zavod za zdravstveno varstvo Maribor – Inštitut za varstvo okolja.

Okoljski vpliv prašenja s terminala koprskega pristanišča za razsuti tovor na kmetijska tla

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IZVLEČEK: Območja okrog pristanišč lahko prizadenejo različni škodljivi vplivi okolja. V pristanišču Koper so ob močni burji pretovarjali hematit, ki je zaradi nenamernega prašenja, prekril širše območje. Ker smo tla koprskega zaledja predhodno že geokemično kartirali, je ponovno vzorčenje omogočilo primerjavo geokemične sestave tal. Onesnaženja nismo ugotovili. Obogatitveni faktorji celo kažejo znižanje vsebnosti večine prvin. Z oddaljenostjo od vira prašenja vsebnosti SiO_2, Na_2O in Cr padajo, Fe_2O_3 naraščajo. Vsebnosti SiO_2 in Cr so pogojene s kopičenjem s kremenom bogatega peska in raztapljanjem karbonata bližje morju. Co in Ni sta verjetno vezana na glinene minerale. Cu, Pb in Zn so lahko delno antropogeno povišani.

KLJUČNE BESEDE: onesnaženje tal, sljudnati hematit, prašenje, pristanišče, severno Jadransko morje, Luka Koper, Slovenija

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NASLOVI :
dr. Nina Zupančič
Univerza v Ljubljani, Naravoslovnotehniška fakulteta, Oddelek za geologijo
Aškerčeva cesta 12, SI – 1000 Ljubljana, Slovenija
in
Paleontološki inštitut Ivana Rakovca
Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
Novi trg 2, SI – 1000 Ljubljana, Slovenija
E-pošta: nina.zupancic@ntf.uni-lj.si

dr. Aleksander Horvat
Paleontološki inštitut Ivana Rakovca
Znanstvenoraziskovalni center Slovenske akademije znanosti in umetnosti
Novi trg 2, SI – 1000 Ljubljana, Slovenija
E-pošta: ahorvat@zrc-sazu.si

dr. Simona Skobe
Univerza v Ljubljani, Naravoslovnotehniška fakulteta, Oddelek za geologijo
Aškerčeva cesta 12, SI – 1000 Ljubljana, Slovenija
E-pošta: simona.skobe@ntf.uni-lj.si

1 Uvod

Morska pristanišča so glavna vozlišča gospodarske dejavnosti in hkrati onesnaževanja okolja na poseljenih obalnih območjih (Bailey in Solomon 2004). Pristaniške dejavnosti lahko pomembno vplivajo na lokalne skupnosti ter na morske in kopenske ekosisteme v regiji. Vplivi segajo od povečanega tveganja za nastanek raka, do onesnaženja vodnih teles in tal (Bailey in Solomon 2004).

Glavni onesnaževalci zraka, povezani s pristaniškimi dejavnostmi, so dizelski izpušni plini, trdni delci (PM), hlapne organske spojine (HOS), dušikovi oksidi (NOx), ozon in žveplovi oksidi (SOx). Ostali problematični onesnaževalci zraka, ki izhajajo iz pristanišč, so ogljikov monoksid (CO), formaldehid, težke kovine, dioksini in pesticidi za fumigacijo pridelkov (Bagley s sod. 1996; Bailey in Salomon 2004; Sharma 2006). Večina člankov, ki obravnavajo vplive pristaniške dejavnosti, je usmerjenih v raziskave učinka izpušnih plinov ladij (Saxe in Larsen 2004; Tzannatos 2010) in v raziskave onesnaženja morskih sedimentov ter živih organizmov (Solis-Weiss s sod. 2004; Adamo s sod. 2005; Cukrov s sod. 2011).

Manj je znanega o učinkih prašenja s terminalov za razsuti tovor na tla. Do emisij lahko pride zlasti med prekladanjem tovora. Učinek prašenja je neposredno viden in zato pogosto glavni vzrok preplaha. Nesreče z raznašanjem tovora, ki vsebuje škodljive snovmi, vplivajo na okolje. Resnost onesnaženja je odvisna od narave snovi ter količin in koncentracij sproščenih v okolje (Internet 1).

Severna jadranska obala je bila poseljena že v času Rimljanov. Od nekdaj so bila naselja odvisna od kmetijstva, vinogradništva, ribolova in trgovine. Še danes na tem območju pridelajo precej zelenjave in grozdja. Z razvojem pristanišča se je pojavil nov vir onesnaževanja, ki lahko vpliva na vsebnost težkih kovin v tleh. Številni avtorji (npr. Aubert in Pinta 1977; Kabata–Pendias in Pendias 1984; Alloway 1990; Adriano 2001; Zupan, Grčman in Lobnik 2008; Andjelov 2012) so z različnih vidikov raziskovali onesnaženje tal v Sloveniji in v tujini, a se njihove študije niso osredotočile na pristanišča kot možni vir potencialno toksičnih prvin.

Luka Koper je večnamensko pristanišče v slovenskem delu severnega Jadrana. Je vstopna točke za blago namenjeno v Evropsko unijo. Na terminalu za minerale pretovarjajo minerale, industrijske minerale in ostali razsuti tovor, predvsem boksit, boraks, cement, fosfate, ilmenit, klinker, perlit, magnezitni sinter, odpadke in podobno (Internet 2).

Pristaniške dejavnosti v ozračje izpuščajo različne snovi. V zraku se lahko med pretovarjanjem razsutih tovorov dvigne predvsem koncentracija prahu. Za suho vetrovno vreme zato veljajo posebni ukrepi (internet 3).

Kljub temu je marca 2011 zaradi zelo močne burje, ki je pihala s hitrostjo 7,3 m/s, med pretovarjanjem razsutega tovora prišlo do neželenega prašenja. Zavod za zdravstveno varstvo Maribor je ocenil, da se je v štirih dneh v zrak sprostilo 1000 kg prahu (Žerjal 2011). Prah železovega oksida je prekril Koper z okolico. Družba je objavila varnostni list, ki ga je predložil lastnik blaga, iz katerega je bilo razvidno, da je tovor v skladu z mednarodnimi standardi. Material, s trgovskim imenom MIOX®, je fiziološko neškodljiv naravni sljudnati hematit (α-Fe_2O_3), ki ga uporabljajo v protikorozivnih in dekorativnih barvah, plastiki, gumi in keramični industriji (Internet 4). Kljub temu so nekateri predstavniki javnosti trdili, da je prah strupen, ker so neuradni rezultati analiz pokazali, da ne vsebuje le železovega oksida, temveč tudi magnezij, aluminij, kobalt in nikelj (internet 5).

V letu 2008 smo v zaledju Kopra izvedli študijo ocene vpliva štirih glavnih možnih virov onesnaženja tal: pristaniške dejavnosti, vinogradništva, kemične tovarne in kmetijstva (Zupančič in Skobe 2014). Ti podatki so tako lahko predstavljali vrednosti ozadja vsebnosti težkih kovin v tleh.

V pričujočem prispevku smo ocenili vpliv prašenja iz leta 2011 na geokemično sestavo in onesnaženja tal.

2 Materiali in metode

Za topografijo širšega območja koprskega pristanišča je značilno hribovito zaledje, razvito na eocenskih karbonatnih flišnih kamninah ter holocenski poplavni ravnici Rižane in Badaševice (Pleničar s sod. 1973). Matična podlaga tal izhaja iz preperelih flišnih kamnin, na katerih so se razvila evtrična tla (TIS / ICPVO 1990–2015).

Tla smo po nenamernem prašenju leta 2011 vzorčili na istih lokacijah kot v letu 2008 (slika 1). Zaradi gradbenih del na treh lokacijah v bližini pristanišča, vzorčna mesta žal niso bila več dostopna. V študiji leta 2008 (Zupančič in Skobe 2014) smo vzorčne lokacije določili glede na rabo tal (kmetijstvo (N1 – N6), vinogradništvo (V1 – V6), bližina pristanišča (L1 – L3) in kemične tovarne (K1 – K6)). Mikrolokacije smo izbrali po načelih naključnega vzorčenja (Davis 1986). Analiziranih je bilo 21 vzorcev vrhnjega dela (15 cm) tal, teže 1,5–2 kg. Po pedološki karti (TIS/ICPVO 1990–2015) so tla iz bližine pristanišča gleji (evtrični glej (IUSS 2014)), razviti na naravnih in delno umetno nasutih morskih in rečnih sedimentih lokalnega flišnega izvora. Vzorci vinogradniških tal (V1 – V4) iz lokacij, ki jih upravlja vinarsko podjetje, so odvzeti na pobočjih. Tip tal so globoko obdelana (rigolana) tla (evtrična rjava (arična) (IUSS 2014)), razvita na eocenskem flišu. Tla vzorčena v dveh zasebnih vinogradih (V5, V6) v bližini kemične tovarne in tla vzorčena na kmetijskih zemljiščih so aluvialna, razvita na flišni naplavini (evtrična obrečna tla (IUSS 2014)).

Slika 1: Lokacije vzorčenja tal na območju Kopra. Legenda: 430 – globoko obdelana (rigolana) tla, evtrična, 100 %; 1086 – aluvialna tla, evtrična, globoka, na ilovnatem aluviju, 60 % in aluvialna tla, evtrična, globoko oglejena, na ilovnati naplavini, 40 %; 1186 – glej, evtričen, mineralen, srednje močen, 50 % in glej, evtričen, mineralen, zmerno močen, 50 % (pedološka karta po TIS / ICPVO 1990–2015).

Glej angleški del prispevka.

Vzorce tal smo posušili na zraku, zmleli, četrtinili in presejali na zrnavost < 0,063 mm, tako da smo dobili 20 g posameznega vzorca. Kemično sestavo vzorcev so izmerili v laboratoriju ACME v Kanadi. Vsebnost glavnih oksidov in nekaterih slednih prvin so analizirali z ICP–emisijsko spektrometrijo: 0,2 g vzorca so razklopili z litijevim metaboratom/tetraboratom in razredčenim dušikovim razkrojem. Ognjevzdržne prvine so določili z ICP–masno spektrometrijo po enakem razklopu. Izguba pri žarenju (LOI) je razlika v teži po žarjenju pri 1000 °C. Skupni ogljik (TOT/C) in žveplo so določili z metodo Leco. Vsebnost plemenitih in navadnih kovin so analizirali z ICP–masno spektrometrijo, tako da so 0,5 g vzorca razklopili z zlatotopko. Točnost in natančnost analitike ter meje določljivosti smo ocenili kot dobre za večino prvin, razen Ag, As, Be, Cd, Hg, Mo, Se, Sb, Sn, Tl in W, ki smo jih zato izvzeli iz nadaljnje razprave.

Normalnost porazdelitve podatkov smo testirali vizualno s histogrami in grafi normalne verjetnosti, s primerjavo aritmetična sredine, geometrične sredine in mediane, s preskušanjem zamaknjenosti in koničavosti ter s Shapiro-Wilkovim testom kot ga predlaga Madansky (1988). Bolj simetrične porazdelitve podatkov smo dosegli z Box-Cox transformacijo (Box in Cox 1964). Statistične teste so za vse spremenljivke izračunane s transformiranimi podatki, vendar so opisne statistike in grafične ilustracije prikazane s surovimi podatki.

3 Rezultati in razprava

Opisne statistike za vse prvine in za obe leti vzorčevanja so zbrane v preglednici 1.

Vsebnosti »strupenih« prvin, poleg Fe, tudi Mg, Al, Co in Ni, bi se morale zaradi prašenja zvišati. Vendar primerjava geokemičnih analiz tal s statističnim t-testom, ni pokazala nobenih statistično značilnih razlik v vsebnosti prvin med letoma 2008 in 2011. Izjema je Co, katerega vsebnost je bila leta 2011 povprečno celo 2 mg/kg nižja. To kaže, da prašenje ni vplivalo na kemično sestavo vrhnjih horizontov tal. Povprečne vrednosti Al_2O_3, MgO in Cr so v obeh letih podobne, a je v letu 2011 razpon vrednosti celo manjši. Po prašenju so izmerjene povprečne vrednosti Fe_2O_3, Co, Cu, Pb in Zn nižje, variabilnost vrednosti pa je ostala podobna.

Glede na stanje pred prašenjem vse težke kovine (razen Cr) in nekatere glavne prvine, vključno z Fe_2O_3, kažejo nekoliko nižje srednje vrednosti (preglednica 1). Mediane vsebnosti prvin v posameznem letu so si še bolj podobne, ker nanje ne vplivajo ekstremne vrednosti oziroma onesnaženi vzorci.

Nizki variacijski koeficienti (CV) pomenijo naravno variabilnost, medtem ko visoki kažejo na antropogeno uvedene vire spremenljivosti. Za večino prvin se je vrednost CV v letu 2011 znižala. Tudi v primerih, ko so se vrednosti CV povišale – Co in Cr le okoli 10, za Ni in Zn okoli 20 ter za Cu in Pb približno 30, lahko to razložimo z naravnim ozadjem in delnim antropogenim prispevkom.

Čeprav nismo ugotovili razlik v vsebnosti prvin v tleh vzorčenih pred in po naključnem prašenju sljudnatega hematita, bi lahko obstajale razlike v njihovi vsebnosti glede na to, koliko so vzorčne lokacije oddaljene od vira prašenja. Območje smo zato razdelili v tri cone oddaljenosti od terminala za razsuti tovor, in sicer: < 1,5 km (L2, L3), 3–3,5 km (N1 – N6 in V3 – V6) in 3,5–4 km (K1 – K6 in V1 – V2). Analiza variance je pokazala 95 % verjetnost razlik v vsebnosti SiO_2, Na_2O, MnO, LOI, C/TOT in Cr glede na oddaljenost od pristanišča.

Preglednica 1: Opisne statistike glavnih prvin (%) in težkih kovin (mg/kg) za leto 2008 (prva vrstica), in leto 2011 (druga vrstica). LOI – žaroizguba, TOT/C – skupni ogljik.

	aritmetična sredina	geometrična sredina	mediana	minimum	maksimum	standardni odklon	variacijski koeficient
SiO_2	53,0	52,8	51,9	44,7	63,2	4,68	8,8
	52,8	52,7	51,4	45,7	64,5	4,59	8,7
AlO_3	10,0	9,9	10,0	8,4	11,8	0,99	10,0
	10,1	10,1	10,2	9,0	11,4	0,82	8,1
Fe_2O_3	4,4	4,4	4,3	3,7	5,1	0,40	9,1
	4,3	4,3	4,3	3,8	4,9	0,33	7,8
MgO	1,4	1,4	1,4	1,0	2,8	0,35	24,6
	1,4	1,4	1,4	1,2	1,6	0,11	8,3
CaO	10,7	10,3	11,1	4,1	14,2	2,66	24,9
	10,9	10,6	11,8	4,6	14,0	2,40	22,0
Na_2O	0,9	0,9	0,9	0,7	1,1	0,08	8,2
	1,0	1,0	1,0	0,8	1,1	0,081	8,2
K_2O	1,607	1,7	1,7	1,4	2,1	0,16	9,6
	1,7	1,7	1,8	1,5	2,1	0,16	8,9
TiO_2	0,6	0,6	0,6	0,5	0,7	0,05	8,9
	0,6	0,6	0,6	0,5	0,7	0,04	7,1
P_2O_5	0,17	0,17	0,17	0,13	0,25	0,04	21,1
	0,17	0,17	0,18	0,08	0,24	0,04	23,6
MnO	0,11	0,10	0,11	0,05	0,13	0,017	15,7
	0,11	0,10	0,11	0,06	0,13	0,02	20,8
LOI	16,8	16,6	17,5	11,8	20,5	2,58	15,3
	16,7	16,6	17,2	10,8	20,2	2,20	13,2
C/TOT	4,0	3,8	4,0	1,8	5,7	0,99	24,9
	3,9	3,8	4,0	1,7	4,9	0,77	19,7
Co	18,1	18,0	18,1	14,3	20,9	1,63	9,0
	16,6	16,6	17,0	13,5	18,7	1,56	9,4
Cr	216,6	214,7	212,3	178,1	315,1	30,28	14,0
	221,1	219,6	219,2	184,9	294,5	27,49	12,4
Cu	51,5	46,8	44,9	31,8	180,90	31,66	61,4
	44,4	42,9	40,1	29,8	77,8	12,73	28,7
Ni	80,3	80,0	80,2	64,0	91,8	6,40	8,0
	78,9	76,4	82,5	47,8	95,0	14,65	18,8
Pb	18,6	18,2	17,4	13,4	30,3	4,14	22,2
	16,5	15,6	17,6	7,0	26,2	4,82	29,2
Zn	71,5	67,9	64,0	57,0	212,0	32,91	46,0
	66,7	65,1	67,0	40,0	105,0	14,57	21,8

Iz slike 2 je razviden padajoči trend vrednosti SiO_2, Na_2O in Cr od pristanišča proti notranjosti ter nekoliko manj prepričljiv trend padanja za Pb in Zn. Za SiO_2, Na_2O in Cr je razlog lahko njihova visoka vsebnost v peščeni frakciji aluvija (Zupančič in Skobe 2014). Porazdelitveni trend Pb in Zn je težje ločljiv, zaradi precejšnjega razpona vsebnosti, ki je verjetno posledica naravne variabilnosti tal, napake vzorčenja in/ali analitike ali še kakšnega drugega razloga. Višje vrednosti bližje pristanišču tako lahko pripišemo onesnaženju z izpušnimi plini vozil, ladij in različnih strojev, ki jih uporabljajo v pristanišču (Fröhling in Ludzay 2002; Kummer s sod. 2009). Trendi Cu in Ni so lomljeni – vrednosti so blizu pristanišča nekoliko nižje kot v območju 3–3,5 km in znova padajo v najbolj oddaljenem pasu. Porazdelitev Cu morda odraža nekoliko povišane vsebnosti v vinogradih (Baker in Senft 1995; Besnard s sod. 2001; Rusjan s sod. 2006). Pri Ni je lahko razlog njegova visoka naravna variabilnost.

Slika 2: Srednja vrednost (točka) in razpon (minimum – maksimum) vrednosti SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, LOI, C/TOT (v %), Co, Cr, Cu, Ni, Pb in Zn (v mg/kg) v letu 2011 v treh različnih conah oddaljenosti (v km) od pristanišča.
Glej angleški del prispevka.

Zviševanje vsebnosti Al_2O_3, MgO, CaO, LOI in C/TOT proti notranjosti odraža mineralno sestavo tal (Zupančič in Skobe 2014). Bližje morju je v tleh več s kremenovim peskom bogate frakcije ter manj karbonata in glinene frakcije (slika 1). Variabilnost in srednja vrednost Al_2O_3 sta najnižji najbližje pristanišču, kar potrjuje, da prašenje iz terminala ni vplivalo na izmerjeno vsebnost. Trend porazdelitve Co je enak, a kaže v vseh treh območjih zelo širok razpon vrednosti. Razen tega tudi vsebnosti Fe_2O_3 naraščajo od pristanišča proti zaledju, kar ne potrjuje vpliva prašenja hematita na kemizem tal.

Obogatitveni faktorji (EF) »kritičnih« prvin (Al_2O_3, Fe_2O_3, MgO, Co, Cr, Cu, Ni, Pb, Zn), izračunani kot razmerje med koncentracijami izmerjenimi po prašenju v letu 2011 in pred njim v letu 2008 (Manta s sod. 2002, Acosta s sod. 2009), so predstavljeni v preglednici 2. Kadar je EF večji od ena, je koncentracija kovine višja od lokalne vrednosti ozadja in kaže na antropogeni vpliv (Luo s sod. 2012). Očitno je, da obravnavani elementi na različnih lokacijah nimajo enakega vzorca. Praviloma so osiromašitve večje od obogatitev, EF pa so tako majhni, da jih je mogoče pripisati naravni ali analitski spremenljivosti in ne onesnaženju zaradi prašenja.

Hematit kopljejo v rudniku Waldenstein v Avstriji (Internet 3). Metamorfni skrilavci koralmskega kristaliničnega kompleksa so orudeni z žilnim tipom mineralizacije. Hematit vsebuje > 92 % Fe_2O_3, do 6 % TiO_2 in manjše vsebnosti MnO ter V_2O_3. V kloritno-hematitni rudi je lahko okoli 6 % Al_2O_3, 3,5 % MgO in 4 mg/kg Ni (Prochaska s sod. 1995). Zato ni presenetljivo, da posamezni delci prikamnine v rudi prispevajo k povišanju Al_2O_3 in MgO, ki so ju v medijih označili kot »nevarne«. Hematit sam je precej inerten. Ni in Co sta lahko v manjših količinah prisotna tudi v rudi, kjer nadomeščata Fe v hematitovi kristalni rešetki. V taki obliki sta za ljudi neškodljiva.

Preglednica 2: Obogatitveni faktorji (EF) izbranih prvin za vse lokacije, razvrščene v naraščajoči oddaljenosti od pristanišča. Obogatene vrednosti so označene z odebeljenim tiskom.

	Al_2O_3	Fe_2O_3	MgO	Co	Cr	Cu	Ni	Pb	Zn
L1	0.98	0.88	0.44	0.85	**1.21**	0.21	**1.06**	0.62	0.33
L2	**1.10**	**1.11**	**1.15**	**1.14**	1.00	0.77	**1.12**	0.97	**1.07**
L3	**1.03**	0.98	**1.03**	0.97	0.93	0.59	**1.08**	**1.06**	**1.09**
N6	0.96	0.93	**1.13**	0.88	0.83	**1.16**	**1.12**	0.87	**1.26**
V4	**1.02**	0.91	**1.08**	0.76	0.97	**1.40**	**1.16**	**1.12**	**1.23**
N3	**1.04**	**1.02**	**1.02**	**1.04**	**1.07**	**1.17**	**1.05**	**1.07**	**1.10**
N5	0.98	0.93	0.88	0.93	**1.03**	**1.04**	0.93	0.82	**1.02**
V5	**1.05**	0.97	**1.05**	0.92	**1.10**	**1.18**	**1.03**	**1.04**	**1.11**
V6	**1.08**	**1.01**	**1.08**	**1.03**	1.00	0.63	**1.06**	0.80	1.00
N1	0.98	0.91	0.95	0.94	**1.15**	0.91	0.97	0.96	**1.02**
N4	**1.01**	0.98	**1.01**	0.92	1.00	0.77	0.67	0.37	0.62
N2	**1.10**	**1.07**	**1.11**	**1.02**	**1.06**	**1.04**	**1.17**	**1.15**	**1.16**
V3	0.98	0.92	0.98	0.79	**1.08**	**1.09**	**1.02**	**1.12**	**1.11**
V1	**1.02**	0.95	**1.09**	0.79	0.94	**1.36**	**1.05**	**1.08**	**1.16**
V2	**1.05**	0.97	**1.03**	0.91	**1.15**	0.59	0.58	0.52	0.63
K3	0.98	1.00	0.97	0.90	**1.07**	**1.09**	**1.08**	**1.13**	**1.10**
K4	0.95	0.92	1.00	0.88	0.94	**1.02**	0.53	0.67	0.67
K2	0.98	0.95	0.94	0.73	1.00	**1.17**	**1.03**	**1.02**	**1.19**
K1	**1.08**	0.97	**1.08**	0.95	**1.03**	**1.27**	**1.09**	**1.14**	**1.14**
K5	0.97	0.94	0.94	**1.02**	**1.04**	1.00	0.99	0.98	**1.23**
K6	**1.06**	**1.03**	**1.02**	**1.05**	0.97	**1.08**	0.70	0.39	0.79

Združeni podatki obeh let (lokacija L1 je izvzeta, ker so 2008 ugotovljeno onesnaženje očitno sanirali) omogočajo pristop z multivariatnimi statističnimi metodami (Swan in Sandilands 1995). Trije faktorji, izračunani na podlagi analize glavnih komponent, pojasnjujejo skoraj 70 % celotne variabilnosti. Nerotirane faktorske obremenitve ločujejo geološke in antropogene vplive. Prvi faktor je visoko obremenjen z SiO_2,

Na_2O in Cr ter odraža visoko vsebnost kremena, povezano z višjo količino peščene frakcije v vzorcih bližje morju. Skladno s tem je ta faktor, zaradi nizke vsebnosti kalcita, visoko negativno obremenjen s CaO, LOI in C/TOT. Drugi faktor odraža vsebnost glinenih mineralov (visoko pozitivni Al_2O_3, Fe_2O_3, MgO, K_2O, TiO_2). Kaže, da sta Co in Ni vsaj delno vezana nanje. Na tretjem faktorju so združene težke kovine Cu, Ni, Pb in Zn, pri čemer so Co, P_2O_5 in MnO negativno obremenjeni. Navedene skupine mineralov/prvin prikazuje slika 3. Možen antropogeni vir Zn in Pb je lahko promet, saj je nekaj Pb prisotnega tudi v neosvinčenem in dizelskem gorivu (Fröhling in Ludzay 2002; Kummer s sod. 2009), nekoliko Zn pa vsebujejo tudi pnevmatike (US EPA 1979). Izvor Cu je lahko dvojen: uporaba fungicidov v vinogradih (Besnard s sod. 2001; Rusjan s sod. 2006) in vpliv prometa (Cadle s sod. 1997). Visoka vsebnost Ni je lahko naravna (Zupančič in Skobe 2014) ali, vsaj delno, posledica zgorevanja goriva iz stacionarnih virov (Pacyna s sod. 2007).

Slika 3: Faktorske obremenitve glavnih prvin in težkih kovin v tleh iz zaledja pristanišča vzorčenih v letih 2008 in 2011. Lokacija L1 je izključena.
Glej angleški del prispevka.

4 Sklep

Leta 2008 vzorčena tla, razvita na aluviju karbonatnih flišnih kamnin, so omogočila oceno možne povišane vsebnosti težkih kovin, do katere bi lahko prišlo zaradi nenamernega prašenja. Leta 2011 je namreč pri pretovarjanju hematita ob zelo močni burji (7,3 m/s) iz Luke Koper odpihnilo 1000 kg materiala. Neuradni rezultati kemijske analize so pokazali, da je bilo poleg železa v prahu tudi nekaj Al, Mg, Co in Ni. Nekateri predstavniki javnosti so trdili, da je prah onesnažil okolje in je škodljiv prebivalstvu.

Po naših raziskavah je zaporedje količine prvin enako v obeh vzorčnih nizih in značilno za tla, nastala na flišnih kamninah bogatih s Cr in Ni.

Edina prvina s statistično različno vsebnostjo med obravnavanima letoma je Co, a je njegova vsebnost po prašenju celo nižja kot pred njim. Ugotovljene povprečne vrednosti Al_2O_3, MgO in Cr so ostale podobne, povprečne vsebnosti Fe_2O_3, Co, Cu, Ni, Pb in Zn so v letu 2011 nižje. Glede na mediano so razlike v vsebnostih prvin med obema vzorčenima letoma še manj izrazite. Za večino prvin (Al_2O_3, Fe_2O_3, K_2O, CaO, MgO, TiO_2, LOI, C/TOT, Cr, Cu, Zn) se je vrednost CV med obema letoma znižala, za nekatere od njih se je povečala (P_2O_5, MnO, Co, Ni, Pb). Kljub temu so vrednosti CV za Co in Cr le okoli 10, za Ni in Zn okoli 20 ter za Cu in Pb približno 30, kar kaže na večji geogeni in manjši antropogeni vir težkih kovin.

Primerjava treh con, od terminala za razsuti tovor oddaljenih < 1,5 km, 3–3,5 km, in 3,5–4 km, je pokazala razlike v vsebnosti SiO_2, Na_2O, MnO, LOI, C/TOT in Cr. Srednje vrednosti SiO_2, Na_2O, Cr, Pb in Zn se z večanjem razdalje od pristanišča zmanjšujejo. Za SiO_2, Na_2O in Cr je lahko razlog njihova koncentracija v peščeni frakciji aluvija in posledično v tleh razvitih na njem. Za Cu in Ni so vrednosti nižje blizu pristanišča, višje v 3–3,5 km coni in spet nižje v najbolj oddaljenem območju. Porazdelitev Cu morda odraža uporabo fungicidov v vinogradih. Spremenljivost vsebnosti Ni, Pb in Zn je lahko naravna, posledica analitske napake ali človekovega vpliva. Vsebnosti Al_2O_3, MgO, CaO, LOI in C/TOT se proti notranjosti višajo, kar kaže na relativno večjo količino karbonata in gline ter nižjo količino kremena v tleh. Co sledi istemu trendu, a z veliko variabilnostjo. Naraščajoči trend Fe_2O_3 od pristanišča proti zaledju ne podpira trditve o onesnaženju tal zaradi prašenja hematita.

Obogatitveni faktorji dveh lokacij, vzorčenih najbližje pristanišču (L2, L3), kažejo da so v letu 2011 tla nekoliko obogatena z Al_2O_3, MgO, Ni in Zn. Z Fe_2O_3 in Co so tla obogatena v lokaciji najbližji pristanišču (L2) in osiromašena v bolj oddaljeni lokaciji (L3), Pb pa je obogaten v lokaciji L3 in osiromašen v lokaciji L2. Cu je glede na stanje pred prašenjem osiromašen. Vsebnost Cr je ostala skoraj enaka. Obogatitveni faktorji so tam, kjer smo povišanje zaznali, tako majhni, da gre verjetneje za naravno ali analitsko variabilnost in ne za onesnaženje s hematitom.

Železov oksid je naravni material. Hematit kopljejo v metamorfnih kamninah, zato je povsem normalno, da je kemijska analiza prahu zaznala tudi nekaj Al_2O_3, MgO iz prikamnine. Tudi Ni in Co sta lahko v manjših količinah prisotna v rudi, saj nadomeščata Fe v kristalni rešetki hematita. V taki obliki sta za ljudi neškodljiva.

Faktorska analiza združenih podatkov obeh let jasno loči vpliv matičnega materiala od kontaminacije. Prvi faktor interpretiramo kot »razdaljo od morja«. Visoko pozitivno je obremenjen s SiO_2, Na_2O in Cr, kar je posledica kopičenja kremena in peska ter raztapljanja karbonata (CaO, LOI, C/TOT) bližje morju.

Drugi faktor, obremenjen z Al_2O_3, Fe_2O_3, MgO, K_2O in TiO_2, izraža »vsebnost gline«. Verjetno sta tudi Co in Ni vsaj deloma vezana na te minerale. Tretji faktor smo imenovali »težke kovine«. Tretji faktor je pozitivno obremenjen s Cu, Ni, Pb in Zn ter negativno obremenjen s Co, P_2O_5 in MnO. Antropogeni del Zn in Pb je morda posledica prometa motornih vozil. Vir Cu bi bil lahko dvojen: uporaba fungicidov v vinogradih in promet. Vsebnost Ni je naravna ali, vsaj delno, posledica zgorevanja goriva.

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5 Literatura

Glej angleški del prispevka.