

Metal content in street dust as a reflection of atmospheric dust emissions from coal power plants, metal smelters, and traffic

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Abstract Resuspended street dust is a source of inhalable particles in urban environments. Despite contaminated street dust being a possible health risk factor for local population, little is known about the contribution of atmospheric dust emissions and other factors to the content of toxic metals in street dust. The impact of smelting, traffic, and power plants on metal contaminates in street dust is the focus of street dust sampling at 46 locations in the Witbank area (Republic of South Africa). This area is characterized by numerous open-pit coal mines in the Karoo coal basin, which provides a cheap source of energy to numerous metallurgical smelters and iron-works and supplies coal to the coal-fired power plants located nearby. Street dust was collected on asphalt or concrete surfaces with hard plastic brushes, avoiding collecting of possible sand, soil, or plant particles. Chemical analysis was done on the <0.125 mm fraction using inductively coupled plasma mass spectrometry subsequent to total digestion. Exceptionally high

concentrations of metals were detected with concentrations of Fe reaching 17.7 %, Cr 4.3 %, Mn 2 %, Ni 366 mg/kg, and V 4,410 mg/kg. Factor analysis indicates three sources for the pollution. Road traffic which contributes to the high concentrations of Cu, Pb, Sb, and Sn, with the highest impacts detected in the town of Witbank. The second source is associated with the metal smelting industry, contributing to Fe, Co, Mn, and V emissions. The highest factor scores were observed around four metallurgical smelter operations, located in the Ferrobank, Highveld, and Clewer industrial areas. Impact of vanadium smelter to street dust composition could still be detected some 20 km away from the sources. Exceptionally high concentrations of Cr were observed in four samples collected next to the Ferrobank industrial area, despite Cr not being loaded in factor 2. The last source of the pollution is most probably fly ash associated with the coal-fired power plants and fly ash dumps. Elements which are associated with this source are Al, Sr, and Li. This factor is abundant in the coal mining part of the study area.

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Introduction

Street dust is a complex mixture of different materials and can be of natural and anthropogenic origin (Charlesworth et al. 2003). Sources of particles of natural origin include soils, sea salt (Amato et al. 2009), volcanic ash, dust, pollen, plant remains, and smoke from forest fires. Anthropogenic dust particles originate from weathering of construction materials, asphalt or concrete abrasion, demolition or construction activities (Kempainen et al. 2003), traffic (wear of brake pads,

tires, fuel combustion processes, and catalytic converters), home cooking and heating using nonrenewable resources, high-temperature combustion processes and industries, as well as dust related to mining, agriculture, and other sources (Piña et al. 2000). Industrial activities can also be an important source of particles in the street dust, especially in the industrialized countries with lower rate of environmental awareness (Al-Khashman 2004; Manno et al. 2006; Tokaloğlu and Kartal 2006; Zheng et al. 2010 and other studies). Even emissions from small-scale industrial activities (Žibret and Rokavec 2010; Žibret 2012) or mining (Gosar and Šajn 2001; Šajn 2002) can have a significant impact on the chemical composition of street dust.

Street dust is regarded as a sink for dust containing high amounts of toxic metals, especially in urban environments. The majority of toxic metals are found in the fraction between 0.45 and 75 μm (Herngren et al. 2006; Wang et al. 1998). It can also be a major source of inhalable (PM_{10} and $\text{PM}_{2.5}$) particles in ambient air (Amato et al. 2009; Piña et al. 2000; Sutherland 2003) due to it being relatively fine-grained and can therefore be easily remobilized by traffic or other activities (Zheng et al. 2010). Contaminated street dust can therefore pose a health risk, especially to children (Shi et al. 2011), due to metals being highly mobile and can easily enter into the blood stream when ingested (Tokaloğlu and Kartal 2006). Thus, the potential health risk associated with contaminated street dust can be higher than that posed by traffic emissions (Zheng et al. 2010). Under acid rain conditions, elements such as Cd and Zn can easily be dissolved (Duong and Lee 2009). Therefore, the runoff water from urbanized areas can be highly toxic to aquatic organisms (McQueen et al. 2010; Wang et al. 1998; Watanabe et al. 2011). The retention time of elements in street dust is approximately 250 days (Charlesworth et al. 2003). Severe rain storms or street sweeping does not significantly change the concentrations of elements but influences the quantity of dust, which can be remobilized during dry weather conditions (Whiteley and Murray 2003).

This study focuses on the multi-elemental analysis of street dust, which acts as a sink of atmospheric particulate matter and thus reflects the scale of the atmospheric emissions from many different sources. The town of eMalahleni (formerly known as Witbank, which will be used in this manuscript), Republic of South Africa, is the research area. Metal smelters, ironworks, coal mines, and traffic are the dominating land uses and are the main sources of metals in the environment. This study shows that atmospheric dust emissions from multiple sources are reflected in the chemical composition of the street dust in a similar way as in soils (Reimann et al. 2012; Šajn et al. 2011; Teršič et al. 2009, just to mention some recent studies) or attic dust (Alijagić and Šajn 2011; Bačeva et al. 2011; Gosar et al. 2006 and many others) in previous studies.

Description of study area

The town of Witbank in the Mpumalanga Province is situated in the South African Highveld. This hilly plateau is situated 1,500–1,700 m above sea level forming an important watershed where three main river catchments, the Vaal, Olifants, and Pongola rivers, originate.

Witbank is situated in the most important coalfield in the country (the Witbank coalfield), located in the late Carboniferous to late Permian age Karoo Basin. The Witbank coalfield is extensively exploited at numerous open-pit and underground coal mines, contributing more than 80 % of total run-of-mine coal production in South Africa. This area is the third largest coal exporting region in the world. Heavy industries and coal-fired power stations developed in close proximity to the coal mines. The result is that an ecologically sensitive area is heavily polluted by metal smelters, ironworks, coal mines, power plants, and urbanization. The mining and smelting industries, however, provide much needed job opportunities, contributing to poverty alleviation in the region. However, Preston-Whyte and Tyson (1988) drew attention to the high SO_2 emission of the Highveld industrial region. The research from Held et al. (1996) over the period 1988 to 1994 described potential impacts of poor air quality and Bell et al. (2001) drew attention to the environmental impacts of abandoned coal mines, focusing on acid mine drainage, spontaneous combustions, and land subsidence. Highveld coal is also enriched with Cr and Mn, and its mining and combustion (power generation, smelting, and heating) might contribute to the increased levels of Hg, Se, As, Cd, Pb, and Mn in the environment (Wagner and Hlatshwayo 2005). The study of Pone et al. (2007) determined the potential environmental and health impacts of spontaneous combustion of coal in the Witbank coalfield and focused on the various gases produced and particle emissions at coal-fire vents. The acid mine drainage potential for Highveld coals were studied by Pinetown et al. (2007). But there is still a large gap in the knowledge about toxic metal contamination in the area, particularly because of atmospheric dust emissions from different sources.

Dust emissions and sources of metals in the studied area

The most important sources of dust in the studied area are associated with coal mining. In most instances, very few dust suppression and prevention measures are taken by local coal mines. Emissions of black coal dust occur during the excavation, blasting, and transportation of coal. Dust emissions also occur due to improper coal storage with a lack of emission prevention measures. The Highveld coal is characteristically depleted in elements such as As, Cd, Cu, Mo, Pb, Se, Zn, and Sb. Content of Co and Ni is similar to global averages. However, this coal is enriched in Cr and Mn, and

slightly enriched in Co, Ni, V, and Hg (Wagner and Hlatshwayo 2005). Unfortunately, the aforementioned study did not take alkali metals into account.

In the study area, the collapsed mine features resulted in the influx of water and air to the coal layers which exacerbated the propagation of spontaneous combustion. Many burning underground coal fires have been observed in the area contributing to the emissions of gases containing toxic organic and inorganic compounds and dust containing metals, such as Hg, As, Pb, Zn, and Cu (Pone et al. 2007). Due to the availability of good quality and cheap energy sources, an extensive metal smelting industry developed in the area. The largest among them is a steel and vanadium producer (Evraz’s Highveld Steel), a chrome-producing plant (Samancor’s Ferrometals, the largest plant in the world), a low carbon ferrochrome producer (Samancor’s Middelburg Ferrochrome), a copper producer (Thos Begbie Holdings), a stainless steel producer (Columbus Stainless), and a large producer of refined silicomanganese and carbon ferromanganese (Transalloys). All aforementioned plants are located in study area.

The National Environmental Management Air Quality Act (no. 39 of 2004) marked an important change in the approach to air pollution control in South Africa. The new legislation established so-called hot-spot or priority areas where poor

ambient air quality is experienced and specific standards are set. The Highveld Priority Area in Mpumalanga, South Africa was the second priority area initiatively declared due to the poor air quality and elevated levels of criteria pollutants associated with the concentration of industrial and non-industrial sources. It covers 31,106 km², including parts of Gauteng and Mpumalanga provinces, and also the eMalahleni Municipality (including the Witbank coalfield). The total annual emissions of particulate matter (PM₁₀) across this priority area are estimated at 279,630 t. The main contribution was attributed to dust entrainment on mine haul roads (50 %), the primary metallurgical industry (17 %), and power generation (12 %). PM₁₀ displays a seasonal trend. Wintertime peaks and summer minimum values are due to prevailing local weather conditions (DEA 2010). Wind directions during summer periods are characterized by daytime NW winds and nighttime E to SE winds. During winter periods, the temperature inversion across the Highveld area prevents the dispersion of dust particles and aerosols (Scheifinger 1997). The average rainfall varies from 900 mm in the higher lying eastern areas to 650 mm in the west. Rainfall is almost exclusively in the form of showers and thundershowers and occurs mainly in the summer from October to March, with the maximum in January. Winters are typically dry, but some rain does occur.

Fig. 1 The distribution of sampling points and the location of dominant sources of the atmospheric dust in the area (power plants, smelters, traffic, and open-pit coal mines). Samples with names *FB1* and *FB2* indicates the position of Ferobank industrial area

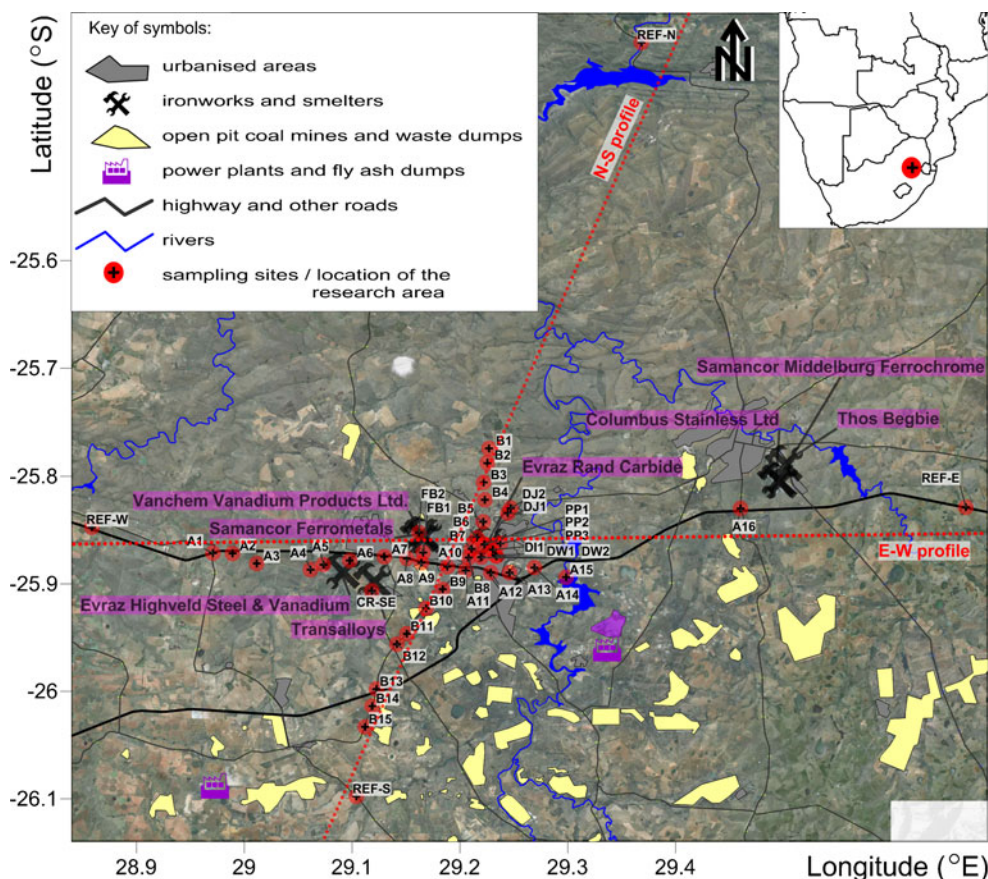


Table 1 Descriptive statistical parameters for chemical composition of street dust in Witbank area

El	U	Min	P25	M	GM	Md	P75	Max	Std	EF	DL	%R	RPD
Al	%	1.15	2.68	3.40	3.25	3.36	4.14	5.76	0.96	0.81	0.01	99	3
Ca	%	0.09	0.35	0.89	0.65	0.67	1.06	4.19	0.84	0.67	0.01	101	3
Fe	%	2.00	4.55	6.29	5.82	5.58	6.97	17.37	2.82	3.10	0.01	103	3
K	%	0.10	0.31	0.52	0.45	0.47	0.71	1.20	0.27	0.43	0.01	98	1
Mg	%	0.10	0.27	0.58	0.47	0.49	0.77	2.04	0.41	0.75	0.01	98	2
Na	%	0.01	0.07	0.11	0.09	0.09	0.14	0.46	0.08	0.09	0.001	96	3
P	%	0.01	0.03	0.04	0.03	0.03	0.04	0.12	0.02	1.10	0.001	95	4
Ti	%	0.25	0.62	1.04	0.88	0.85	1.18	4.50	0.75	5.24	0.001	94	4
As	mg/kg	2.00	5.00	6.95	6.44	7.00	7.00	21.00	3.03	2.80	1	125	10
Ba	mg/kg	55	201	318	270	260	400	1,837	258	0.98	1	95	4
Be	mg/kg	0.50	0.50	1.14	0.98	1.00	2.00	2.00	0.62	1.05	1	N/A	50
Bi	mg/kg	0.10	0.30	0.42	0.37	0.40	0.50	1.00	0.20	5.02	0.1	N/A	20
Cd	mg/kg	0.10	0.10	0.23	0.18	0.20	0.30	0.90	0.18	4.90	0.1	50	34
Ce	mg/kg	27.0	59.0	85.0	78.0	76.0	102.0	185.0	37.2	2.61	1	99	6
Co	mg/kg	7.1	18.1	24.2	22.5	23.2	26.7	63.9	9.9	2.70	0.1	105	3
Cr	mg/kg	299	991	5,250	2,700	3,050	6,360	43,000	7,560	110	1	95	8
Cu	mg/kg	13.8	44.9	73.2	63.0	58.4	79.3	300.3	50.6	5.05	0.1	95	13
Hf	mg/kg	1.40	3.20	3.95	3.78	3.60	4.40	7.10	1.21	1.44	0.1	94	9
Hg	mg/kg	0.005	0.030	0.092	0.044	0.040	0.060	1.710	0.250	3.54	0.01	117	21
La	mg/kg	10.1	21.5	30.4	28.2	29.0	34.3	77.5	13.0	1.90	0.1	106	5
Li	mg/kg	6.4	12.9	16.3	15.4	14.8	20.3	29.3	5.7	1.31	0.1	91	5
Mn	mg/kg	610	1,117	2,264	1,723	1,440	2,143	20,000	2,890	4.38	1	101	4
Mo	mg/kg	1.00	1.90	2.83	2.48	2.45	3.10	12.50	1.97	4.98	0.1	100	10
Nb	mg/kg	4.1	10.1	12.1	11.6	11.1	14.2	22.4	3.8	1.95	0.1	92	7
Ni	mg/kg	19.4	42.0	74.6	61.3	53.0	74.9	366	62.2	3.07	0.1	105	11
Pb	mg/kg	10.8	42.5	89.3	62.8	57.9	81.1	835	126	10.2	0.1	98	16
Rb	mg/kg	7.8	21.3	33.3	29.9	31.5	41.3	70.1	15.1	0.79	0.1	96	3
Sb	mg/kg	0.30	0.90	1.88	1.51	1.50	2.40	7.20	1.37	9.09	0.1	74	18
Sc	mg/kg	3.00	6.00	7.24	6.97	7.00	8.00	15.0	2.09	1.00	1	88	3
Sn	mg/kg	1.80	3.00	5.48	4.68	4.40	7.20	18.5	3.38	5.04	0.1	99	28
Sr	mg/kg	14.0	44.0	66.8	59.0	57.5	81.0	204	35.3	0.40	1	96	5
Ta	mg/kg	0.20	0.60	0.73	0.69	0.70	0.80	1.50	0.24	1.57	0.1	106	16
Th	mg/kg	4.1	11.1	14.7	13.5	13.0	17.4	39.1	6.6	2.71	0.1	102	11
U	mg/kg	1.10	2.40	3.00	2.88	2.90	3.20	5.60	0.89	2.15	0.1	89	11
V	mg/kg	82	179	451	300	246	377	4,410	681	8.99	1	102	4

Table 1 (continued)

El	U	Min	P25	M	GM	Md	P75	Max	Std	EF	DL	%R	RPD
W	mg/kg	0.40	1.00	1.25	1.16	1.10	1.60	2.40	0.47	1.27	0.1	83	17
Y	mg/kg	6.6	14.1	17.1	16.4	16.7	19.4	32.3	4.9	1.57	0.1	104	7
Zn	mg/kg	32.0	99.0	222	162	151	258	1,330	234	6.41	1	95	6
Zr	mg/kg	58	120	145	139	130	167	258	45	1.46	0.1	99	9

Number of samples is 46

El/element, U units, Min minimum, P25 25th percentile value, M mean, GM geometrical mean, Md median, P75 75th percentile value, Max maximum, Std standard deviation, EF enrichment factor, DL detection limit, %R recovery rate of geochemical standard, RPD average relative percent difference of duplicates, N/A no data available

Materials and methods

Street dust was collected along two more or less straight lines in the N-S and E-W direction. These lines are referred to as “profiles” in this manuscript. N-S profile contains samples from REF-N, B1, B2...B15 to REF-S, and E-W profile contains samples from REF-W, A1, A2....A16, to REF-E (Fig. 1). The town of Witbank, where the majority of heavy industry is situated, is located at the center of the study area at the intersection of the two profile lines. Four reference samples were collected from areas located far away (>16 km) from the main pollution sources in each direction. The length of both profile lines is around 80 km with 35 samples collected (18 samples along the E-W direction and 17 samples along the N-S direction). Additional samples were taken in the vicinity of major industrial facilities and in densely populated areas of Witbank. The total number of street dust samples was 46. Figure 1 shows the sampling plan, as well as the locations of major atmospheric dust pollution sources.

Sampling begun with the careful selection of micro-locations to avoid sampling of sand particles, plant remains (leaves, pollen, seeds or similar), or soil and rock material (soil, mud, debris falling from trucks, dirt from wheels, etc.). Larger parking areas, playgrounds, larger road intersections, bridges, or other similar infrastructure were found to be the most suitable surfaces for sampling. After the selection of sampling surface, unwanted coarse-grained material (sand, asphalt remains, etc.) was cleared away with a soft plastic brush after which, electrostatically connected dust particles inside holes and pores in the asphalt or concrete were collected with a hard plastic brush. Fine-grained material was collected and sealed in a plastic bag. Approximately 200 to 500 g of composite sample material was collected from at least 15 different sampling surfaces at each sampling point.

Samples were dried at 303 K for XXX minutes/hours and sieved through a 0.125-mm mesh to obtain the fine-grained fraction. A subsample of 5 g of the <0.125 mm material was used for chemical analysis. Chemical analysis was done at the ACME analytical laboratories, Vancouver, Canada, using inductively coupled plasma mass spectrometry (ICP-MS) after total (four acid) digestion. A total of 41 elements were analyzed using this method, including Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb, and Hf. Only Hg was analyzed using ICP-MS after aqua regia digestion. The accuracy was evaluated with six analysis of geochemical standard material STD OREAS24P (ACME Laboratories internal standard) and the precision with nine repetitions.

Data processing

Elements, where the concentrations were mainly (>30 % of samples) below the detection limit, were discarded from further

Table 2 Comparison of maximum content of selected metals in street dust found in world literature with maximum 75th percentile value (P75) in Witbank area, and with South African soil screening value for standard residential area (EA 2010) and with action values for soil, according to “The New Dutchlist” (Swartjes 1999). All values are in milligrams per kilogram, except for Fe (in percent)

Reference	Pb	Cr	Ni	Mn	As	V	Zn	Fe	Cu	Cd	Co
Wang et al. (2012)	120	200	90	–	55	–	600	6	140	–	–
Yongming et al. (2006)	3,060	853	–	1,318	20	–	2,112	–	1,071	–	–
Tokaloğlu and Kartal (2006)	312	81.2	217	519	–	–	733	–	144	146	–
Charlesworth et al. (2003)	199	–	636	–	–	–	3,164	–	6,688	13	–
Al-Khashman (2004)	314	–	6.5	–	–	–	137	–	84	–	–
Yang et al. (2010)	265	103	45.7	1,123	–	90.3	355	5.35	125	–	–
Kong et al. (2011)	523	160	85	1,552	51	175	3,273	–	197	10	31
Wei et al. (2009)	99	175	96	1,458	–	–	846	–	252	15	25
Khairy et al. (2011)	710	149	59	568	9	102	8,153	3.8	242	7	–
Apeagyei et al. (2011)	1,639	530	–	1,191	–	–	1,208	10	2,130	–	–
Kabadayi and Cesur (2010)	240	–	130	180	–	–	170	–	350	6.5	42
Lu et al. (2010)	1,970	215	219	2,336	43	144	1,778	–	260	–	23
Maximum—this study	835	43,000	366	20,000	21	4,410	1,334	17.4	300	0.9	64
P75—this study	81	6,360	75	2,140	7	377	257	7	79.3	0.3	27
Location of max. value	–	FB2	–	A6	–	A6	–	PP1	–	–	FB2
Soil screening value for standard residential area	230	–	1,200	1,500	48	320	19,000	–	2,300	32	630
Action values for soil	530	380	210	–	55	–	720	–	190	12	240

Maximum values are emphasised in italic

analysis. These elements are Ag, Au, and S. In other cases, where elemental concentrations were not detected, it was assumed to be 50 % of the corresponding detection limit. The concentration was assumed to be the average value of two results in cases where duplicate samples were analyzed for precision testing. Descriptive statistical parameters were calculated using the Statsoft Statistica software package. Quality control parameters are relative percent difference (RPD), which represents precision, and was calculated using the duplicate analyses, and percent recovery rate (%R), which shows accuracy, and was

calculated according to standard analyses. These parameters were calculated according to Eqs. 1 and 2, where CM represents measured concentration, CR means concentration in the repetition, and CS means known concentration in the standard.

$$RPD = \frac{100}{9} \cdot \sum_{n=1}^9 2 \frac{|CM_n - CR_n|}{CM_n + CR_n} \quad (1)$$

$$\%R = \frac{100}{6} \cdot \sum_{n=1}^6 \left(1 + \frac{CM_n - CS_n}{CS_n} \right) \quad (2)$$

Table 3 Factor loadings matrix. Loadings of absolute value larger than 0.7 are in italics

	F1	F2	F3
Sb	0.94	0.01	0.07
Sn	0.89	–0.08	–0.10
Cu	0.86	0.24	0.08
Pb	0.76	0.05	0.26
V	0.06	0.83	–0.18
Fe	0.06	0.83	–0.18
Co	0.22	0.83	0.17
Mn	–0.14	0.81	–0.16
Al	0.05	–0.12	0.93
Li	0.01	–0.24	0.93
Sr	0.11	0.12	0.90
Var variance, loaded in separate factor	28	26	25

In order to detect the elements in the environment around Witbank that are related to anthropogenic activities, enrichment factors (EF) were calculated and related to a “conservative” reference element (Reimann and de Caritat 2005), which should be a naturally distributed element, which is not used or produced in the study area, is not abundant in coal, is not emitted by traffic, and is not abundant in construction materials (cement, bricks, concrete, asphalt, etc). The reference element should also have a low variance, and the concentration thereof in street dust should be of similar magnitude as the average upper crustal abundance. Sc was found to be the most suitable reference element. EFs for street dust in the Witbank area were calculated using average values in street dust and average values for the upper crust (Rudnick and Gao

Table 4 Correlation of element concentrations with factor scores. Correlations, where absolute value is larger than 0.5, are set in italics. Number of samples is 46. Elements, presented in this table, are not included in factor analysis

	F1	F2	F3
Zn	<i>0.56</i>	0.24	0.33
Cd	<i>0.52</i>	-0.05	0.19
Cr	<i>0.50</i>	0.29	-0.07
Na	<i>0.50</i>	0.15	0.28
Ni	0.46	<i>0.55</i>	0.04
Ti	-0.15	<i>0.53</i>	-0.31
Mg	0.42	<i>0.53</i>	0.07
Ba	0.23	-0.04	<i>0.67</i>
P	0.16	-0.31	<i>0.66</i>
Sc	0.00	0.46	<i>0.63</i>
Rb	0.20	-0.30	<i>0.60</i>
K	0.29	-0.24	<i>0.60</i>
As	0.28	-0.19	0.20
Be	-0.03	-0.08	0.49
Bi	0.46	-0.14	0.48
Ca	0.23	0.37	0.24
Ce	0.05	-0.19	0.47
Hf	0.14	-0.20	-0.09
Hg	0.32	0.02	0.40
La	0.06	-0.22	0.49
Mo	0.48	0.22	0.18
Nb	-0.02	-0.36	0.05
Ta	0.11	-0.32	0.30
Th	0.02	-0.30	0.38
U	0.07	-0.29	0.40
W	0.46	-0.05	0.26
Y	0.21	-0.22	0.43
Zr	0.17	-0.20	-0.11

2003) as in Eq. 3. AVe is the average value of the concentration of elements in street dust, AVr is the corresponding value of the reference element in street dust, CCe is the average concentration of elements in the upper crust, and CCr is the corresponding value for a reference element.

$$EF = \frac{AVe/AVr}{CCe/CCr} \tag{3}$$

All further data processing used logarithmic values to assure normal or close to normal statistical distribution. In order to separate possible influences of different pollutants in the area, and to determine the possible geochemical associations of elements, factor analysis was done. Zero-mean unit-variance linear transformation was done prior to factor analysis. Because the number of samples is too low to perform a factor analysis on a complete set of elements, it was done for 11 selected elements by using three factors and Varimax factorial axes rotation. Factor analysis was done according to the procedure, described by Žibret and Šajn (2010). Connection of other elements to a specific factor was determined by the

correlation of elemental concentrations to the factor scores. The evaluation of possible sources of the different elements in the environment was based on the spatial distribution of factor scores and according to the scaling of the content of an element in relation to the distance from the suspected source.

Results and discussion

Descriptive statistical parameters, as well as laboratory quality control parameters and enrichment factors for analyzed elements, are presented in Table 1. The quality control parameters indicate good quality chemical analysis. The average recovery rate for the major elements was found to be within the interval of 90–110 %, suggesting the analyzed values properly represent the real ones. Low recovery rates were recorded for Cd and Sb. This can be attributed to the fact that the concentrations for these elements in the standard are just above the detection limit of the laboratory (i.e., the expected value is 0.15 and 0.09 mg/kg and the detection limit is 0.1 and 0.1 mg/kg for Cd and Sb, respectively) and do not reflect on the quality of the analysis properly. W, Sc, and U show slightly lower than expected recovery rates. Higher than expected recovery rates were recorded for Hg and As. A large (larger than 20 %) average relative percent difference for the duplicate sample analyses was found for Bi, Hg, Sn, Cd, and Be. Be, Bi, Cd, and Hg contents are very low and are near the detection limits, and this might be the reason for lower precision of the chemical analysis. These elements were not used as a reference element and were not used in factor analysis; therefore, such uncertainty does not influence the final conclusions of this study.

Sn was used in factor analysis because the enrichment factor was above 5, which means that the anthropogenic source is present in the Witbank area, despite the lower precision of the detected for the laboratory analyses. However, due to the fact that the accuracy parameter %R showed an excellent recovery rate (99 %), such unwanted sources of noise should not have a significant influence on the final conclusions. Enrichment factors larger than 5 were also detected for Ti, Bi, Cu, Pb, Sb, V, and Zn (Table 1).

Descriptive statistical parameters show that the concentration of some elements in the street dust collected around smelters is extremely high compared to data from other scientific studies conducted around the world. These elemental concentrations outweigh any of the available data on street dust compositions in similar settings. This is especially valid for Cr, Ni, Mn, V, Fe, and Co. The extremely high concentrations detected in this study highlight the severe levels of environmental pollution in the Witbank area. The maximum concentrations of metals in different studies around the world are listed in Table 2 and compared with maximum and 75th percentile values in this study. Locations of sampling positions where extremely high values were

detected give an indication of the possible sources of these metals in the environment. The highest values for Co (64 mg/kg) and Cr (4.3 %) were detected in the Ferrobank industrial area, where the Cr and V smelters are located. The highest values for Mn (2 %) and V (4,400 mg/kg) were detected adjacent to the vanadium slag and steel/alloy plant. Maximum values for Fe (17.4 %) were measured next to the carbide smelter and the highest value for Ni (366 mg/kg) adjacent to another ferrochrome smelter and stainless steel plant closer to the town of Middelburg 4.5 km away from the Ferrobank industrial area. As the Middelburg area was not the focus of this study, unfortunately no sampling was done closer to this particular industrial area. The concentrations of metals in street dust in the vicinity of these smelters therefore remain untested. Although South African soil screening values for residential areas (EA 2010) and action values according to “The New Dutchlist” (Swartjes 1999) cannot be directly compared to the content of metals in street dust, such comparison might give some insight into the scale of the pollution observed in the study area (Table 2). Elements of the biggest concerns are Pb, Cr, Mn, and V, where their maximum values in street dust exceed soil screening values or action values with a factor of 4 (Pb) to more than 100 (Cr).

Factor analysis shows three different geochemical associations of elements in the street dust samples, indicating

three main sources for the anomalies observed. Table 3 shows the factor loadings for 11 selected elements and Table 4 the correlation coefficients of elemental concentrations (logarithmical values) and factor scores for elements which were not included in the factor analysis. Factor 1 represents 28 % of the total variance. Cu, Pb, Sb, and Sn are loaded in this factor. These elements are typically associated with traffic emissions (Gunawardana et al. 2012; Manno et al. 2006; Wei et al. 2009). Source for Cu and Sb is most likely the wear of brake pads (Adachi and Tainosho 2004; Amato et al. 2009; Fujiwara et al. 2011). Despite the fact that South Africa phased out leaded fuel use since 1996, 6 % of the vehicles on South African roads still use leaded fuel; therefore, Pb can be associated with the use of leaded fuel. Closer examination of the spatial distribution of factor 1 scores reveals that the highest factor 1 scores are found in the town of Witbank as well as in samples taken on several bridges crossing N4 highway (linking Pretoria and Nelspruit) (Fig. 2). This suggests that factor 1 can be associated with traffic emissions. Other elements which might be associated with the traffic emissions are Na, Zn, Cd, and Cr (Table 4), due to concentrations are correlated with factor 1 scores.

The distribution of Cr will be discussed at this point. The chrome smelter (Ferrobank industrial area) operates six charge chrome furnaces and is considered a dominant source of Cr. The Ferrobank industrial area is situated to the west of

Fig. 2 Spatial distribution of factor 1 (Sb, Sn, Cu, and Pb) scores, suggesting that traffic is the dominant source of these metals

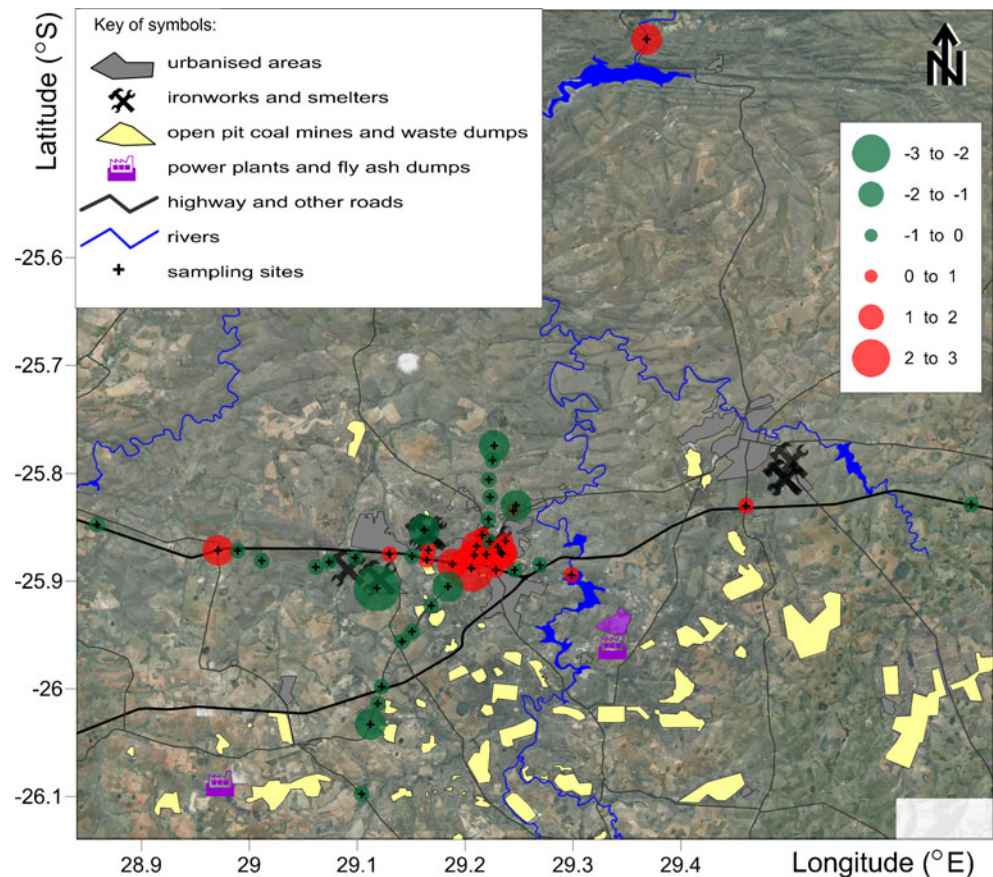
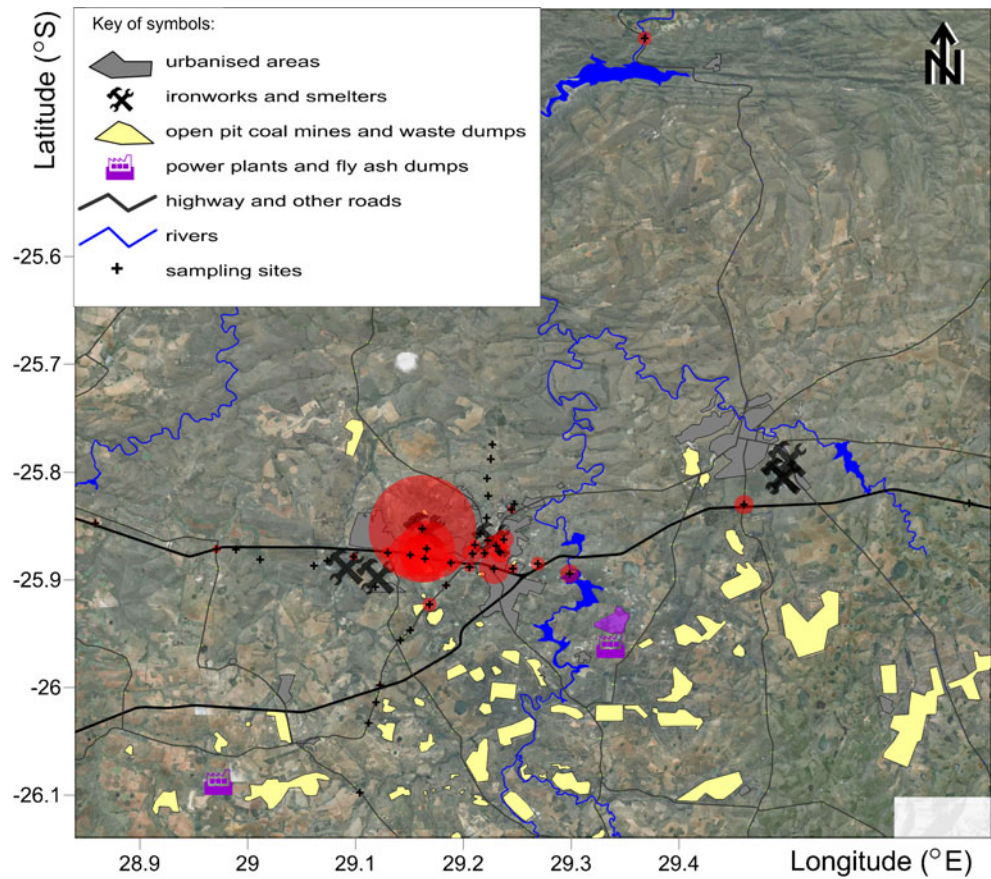


Fig. 3 Spatial distribution of Cr in street dust; the diameter of the circle represents the Cr concentrations; maximum value is 43,000 mg/kg



the town of Witbank (Fig. 1). The spatial distribution of high Cr concentrations in street dust therefore corresponds to areas of high traffic movement. Figure 3 shows the spatial distribution of Cr in street dust, where the extent of the pollution plume can

be estimated. Thus, the source of Cr in street dust is not associated with traffic, but rather with the Cr smelter in the Ferrobank industrial area west of Witbank. This is further proved by the log–log scatterplot of Cr concentration in street

Fig. 4 Log–log scatter plot of Cr concentrations in street dust with the distance from the Samancor Ferrometals plant. Correlation coefficient is -0.52 , and the regression line equation is: $\log(\text{Cr concentration in milligrams per kilogram}) = 4.05 - 0.67 \times \log(\text{distance from Samancor Ferrometals in kilometer})$

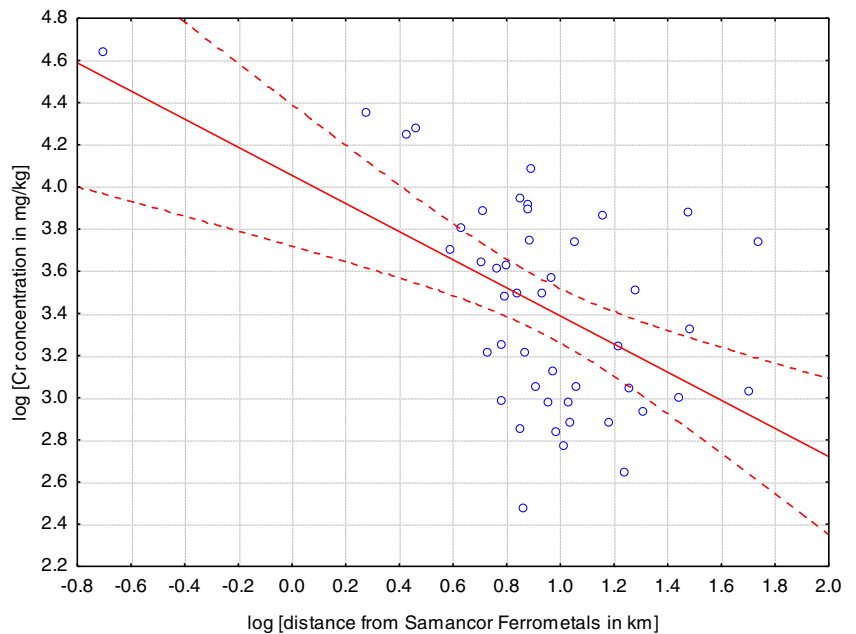
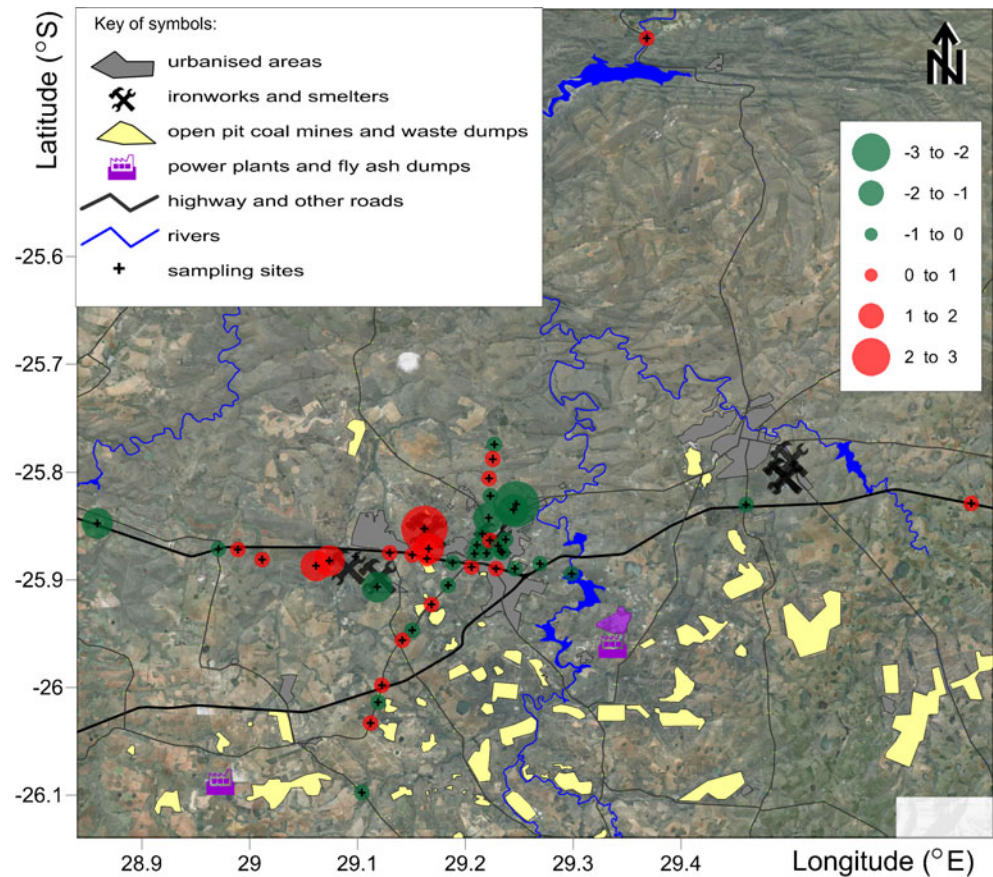


Fig. 5 Spatial distribution of factor 2 (V, Fe, Co, and Mn) scores, suggesting that smelters are the dominant source of these metals



dust and the relation to the distance of the sample sites from the chrome smelter (Fig. 4). A correlation coefficient of -0.52 and a linear regression line equation is $\log(\text{Cr concentration in milligrams per kilogram}) = 4.05 - 0.67 \times \log(\text{distance of sample sites from the smelter in kilometer})$.

Fe, Co, Mn, and V are loaded in factor 2, which explains 26 % of the total variance (Table 3). These elements have been usually linked to the smelting industry (Alijagić and Šajin 2011; Bačeva et al. 2011; Stafilov et al. 2010a, b; Šajin 2005; Šajin 2006), which is also abundant in the Witbank area, in

Fig. 6 Log–log scatter plot of Mn and V concentrations in street dust with the distance from the Evraz Highveld Steel and Vanadium plant and Transalloys plant (both plants are located next to each other) suggested natural background levels and detected range of influence, being 20 km. Correlation coefficient for Mn is -0.69 , and the regression line equation is: $\log(\text{Mn concentration in milligrams per kilogram}) = 3.87 - 0.59 \times \log(\text{distance from the source in kilometer})$. Correlation coefficient for V is -0.73 , and the regression line equation is: $\log(\text{V concentration in milligrams per kilogram}) = 3.29 - 0.76 \times \log(\text{distance from the source in kilometer})$

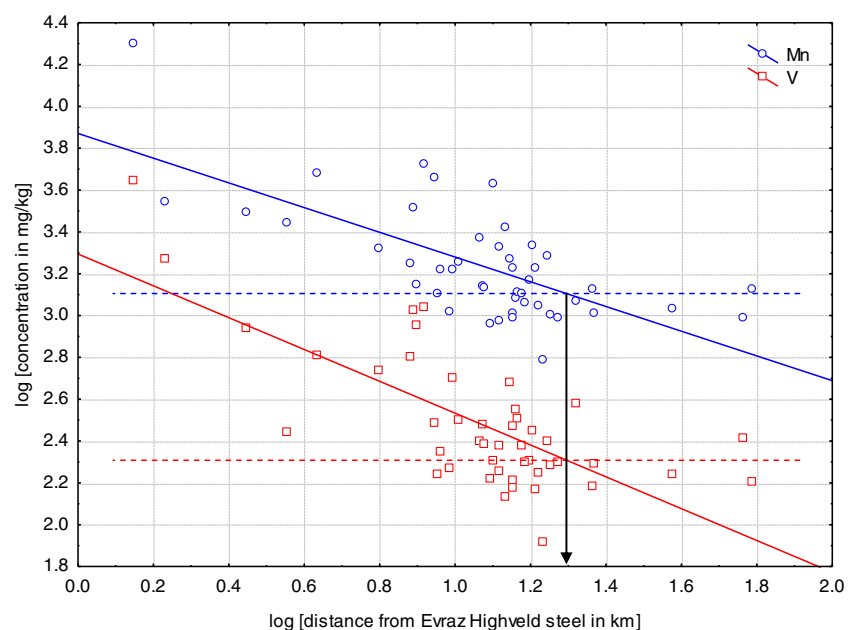
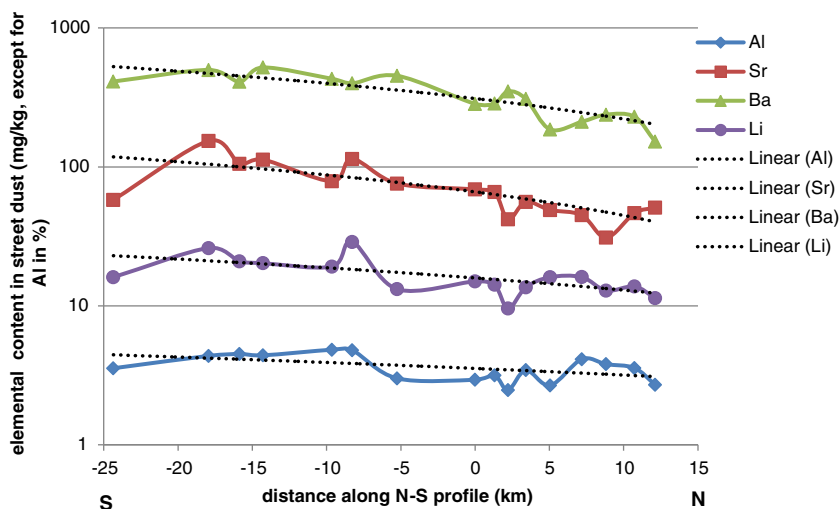


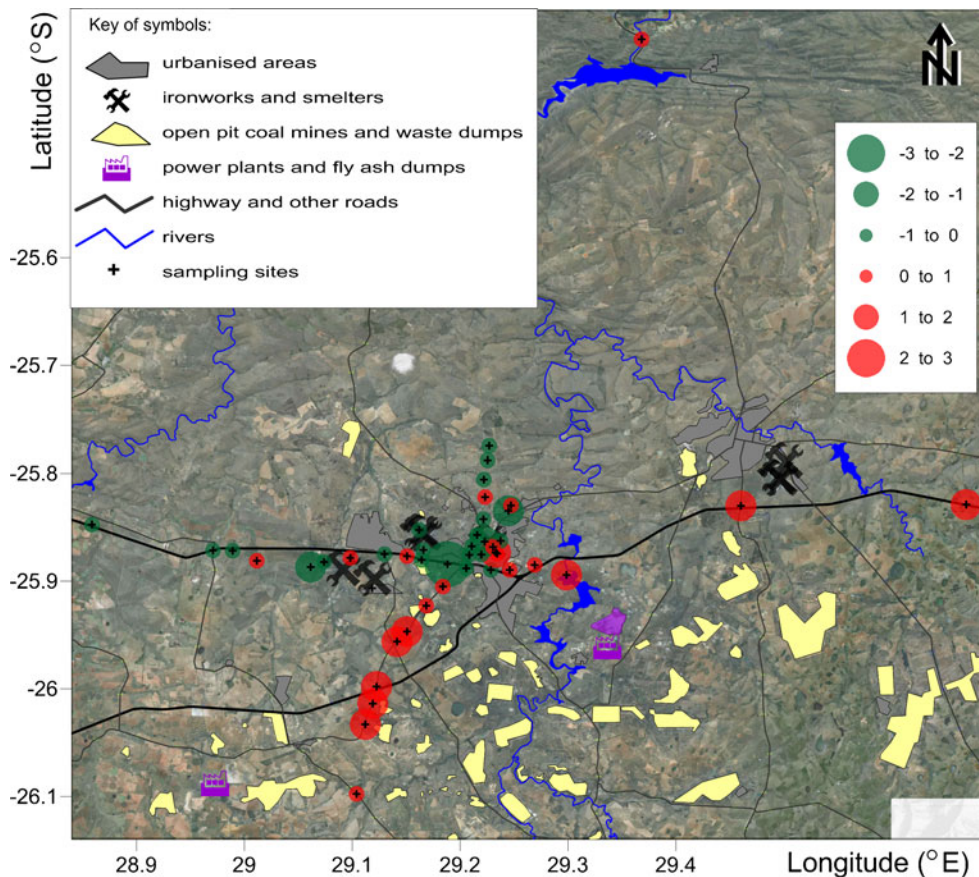
Fig. 7 The content of Al, Sr, Ba, and Li in street dust along N-S profile. Distance 0 indicates the location of Witbank town. Sample REF-N is excluded from this profile because it is located far away to the north



particular in the area to the west of Witbank. Closer investigation of the spatial distribution of factor 2 scores confirms that the Witbank smelting industry is a source for this geochemical association (Fig. 5). The exception is the sample point located south-east of these plants (sample CR-SR), which was depleted in these elements, but this sample contained high proportions of natural eroded and wind-blown soil. A high correlation was found between the distance

of the sample sites from the largest steel plant (Evraz Highveld Steel) and adjacent ferromanganese smelter and the concentrations for both Mn ($r=-0.69$) and V ($r=-0.73$) (Fig. 6). Regression equations are: $\log(\text{Mn concentration in milligrams per kilogram})=3.87-0.59 \times \log(\text{distance of sample from Evraz Highveld Steel in kilometer})$ and $\log(\text{V concentration in milligrams per kilogram})=3.29-0.76 \times \log(\text{distance of sample from Evraz Highveld Steel in kilometer})$.

Fig. 8 The spatial distribution of factor 3 (Al, Li, and Sr) scores, suggesting that coal mining and related activities (power plants) might be the dominant source of these elements



The estimated concentrations of elements in the natural background suggest the range of influence of industrial sources to the composition of street dust to be around 20 km ($\approx 10^{1.3}$). Other elements, which might be associated with the smelting industry, are Ti, Mg, and Ni (Table 4).

Elements, loaded in factor 3, are Al, Sr, and Li. Twenty-five percent of the total variance is explained with this factor. Other elements, which might be associated with this factor, are P, K, Ba, Sc, and Rb (Table 4). All the aforementioned elements (excluding P, Al, and Sc) are alkali or alkaline metals. It is typical for these elements to be enriched in fine particulate matter, produced through the combustion of coal (Takuwa et al. 2006). Figure 7 shows the changes of the content of Al, Sr, Li, and Ba along the N-S profile with the indicated linear regression line. Higher concentrations were observed in the southern part of the study area, where numerous open-pit coal mines and power plants exist, and lower concentrations in the northern part, where coal mining and power plants does not exist. Figure 8 shows the spatial distribution of factor 3 scores. The highest factor 3 scores are, however, located in the southern part of the study area, where open-pit coal mines and power plants (total wattage of five large plants in the area is more than 20 GW) dominate the landscape. Factor 3 can therefore be linked to dust emissions from power generation and fly ash dumps, and possibly also to the dust generation from coal mines. Unfortunately, we did not have data on the alkali element content of the Witbank coals. Therefore, it is not possible to determine whether this factor is indicative of dust mobilized directly during coal mining and transport activity, ineffective filtering systems at coal-fired power plants, or associated with the wind-blown dust from fly ash ponds.

Conclusions

The extent of the pollution associated with coal mining, power generation, smelting industry, and traffic was investigated through street dust sampling, taken along an E-W and N-S profile, around the main suspected pollution sources and in a densely populated area. Maximum detected levels for Cr, Ni, Mn, V, Fe, and Co were much higher than the maximum values recorded in other polluted areas around the world and exceed permitted values for soil for a factor from 4 to more than 100. Three different sources of pollution were shown by factor analysis. The first dominant source of the metals in street dust is traffic, contributing to the contamination of Cu, Pb, Sb, and Sn, and is represented by the factor 1. The highest levels of these elements are found in the Witbank City center and along the N4 highway. The second and most dominant source of the pollution, represented by the factor 2, is the Witbank smelting industry, which produces atmospheric emissions of Fe, Co, Mn, and V. The detected range of influence for one particular Mn and V plant in street dust is

around 20 km. Cr and Co anomaly was also detected around Ferrobank industrial center, which is in the vicinity of densely populated areas. Third geochemical association is represented by Al, Sr, and Li, which is most likely connected to with fine particles released into the atmosphere during coal combustion. According to the spatial distribution of factor 3 scores, large power plants in the southern part of the researched area and open-pit coal mines are suspected to be the source of this factor, but more samples are required to confirm this indication. Detailed inspection of collected samples by SEM/EDS will allow direct identification and evaluation of different sources of particles in this area. Such study can be a direct follow-up of this research.

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