TRAFFIC RELATED METALS AS SOURCES OF URBAN ENVIRONMENT POLLUTION: A CASE STUDY OF KRAKÓW, POLAND

EWA ADAMIEC
AGH University of Science and Technology, Poland

ABSTRACT
The purpose of the research was to extend the current knowledge on traffic related metals in road dust which can be easily released to the environment and cause potential human health risks. Emissions from road traffic consists of exhaust emissions but also non-exhaust ones (wear and tear of vehicle parts, road surface as well as resuspension of dust) and can easily penetrate the air and river systems (runoff and air deposition after resuspension). Samples were taken in Krakow that is a very important transportation hub in southern Poland, characterized by very high traffic, congestion and is a significant tourist destination due to its cultural heritage. Results revealed high concentrations of all investigated metals in all road dust samples collected from traffic polluted sites and they were significantly more contaminated than samples collected from the reference sites. It can be assumed that the metals Cr, Zn, Pb and Cu can pose a significant hazard to the environment. The samples of fine fraction (<20 µm) of road dust were extremely contaminated with all of the investigated metals, in particular with Zn and Cu. Road dust could substantially pollute Vistula. Moreover, monitoring of road environment samples, in particular fine fraction, should be intensified because resuspended fraction easily enters the environment as well as human airways. Chemical analysis of all samples were supplemented with the fractionation study using BCR protocol (Binding Corporate Rules of the Commission of the European Communities). Fractionation studies revealed that mobility of examined metals decreases in that order: Zn>Pb>Cu>Cr. It should be noted, however, that metals even when not mobile in the environment can become a serious health concern when ingested or inhaled.
Keywords: oxidation stress, metals, non-carcinogenic health risk assessment, traffic related elements (TREs), road dust, brake lining, tire, non-exhaust emission, road environment.

1 INTRODUCTION

Road traffic is considered one of the major sources of environmental pollution in urban areas. Air pollution and its huge health and environment impact resulting from traffic, are considered to be the most important target for sustainable transport in EU. The impact of both short term and chronic exposures to particulate matter PM2.5 and PM10 on respiratory and cardiovascular health and consequently on morbidity has been subject to intense studies [1]–[9]. It is unambiguous that long-term exposure to air pollution causes development of multiple health problems and diseases. As reported by Künzli et al. [10], Hoffmann et al. [11], Bauer et al. [12] human exposure to coarse particles (between 2.5 and 10 µm) results in adverse cardiovascular health problem such as atherosclerosis or respiratory endpoints health including premature mortality [13]–[17]. As reported by Loeb [18] oxidative stress is directly linked to several DNA lesions and the formation of bulky adducts, mechanisms by which traffic-related pollution could elicit mutagenesis and cause cancer. Potential general pathophysiological pathways linking particulate matter exposure with cardiopulmonary morbidity and mortality are in details presented in [19].

Human and environment exposures to particles emitted from motor vehicles include complex mixtures of metals from tires, parts wear: systems brakes, clutch plates, the erosion of the active layer of the catalytic converter and resuspended road dust. Since most studies

WIT Transactions on Ecology and The Environment, Vol 214, © 2017 WIT Press
www.witpress.com, ISSN 1746-448X (on-line)
doi:10.2495/ECO170081

on toxicity and health consequences of roadside particulate matter are focusing on exhaust emission, particles from the non-exhaust sources are yet not so well recognized [18]. Potgieter-Vermaak et al. [20] has confirmed that the chemical composition of inhaled and ingested particles plays a major role in its toxic, genotoxic and carcinogenic mechanisms, but the component-specific toxic effects are still not understood. It is unambiguous that long-term exposure to air pollution causes development of multiple health problems and diseases such as atherosclerosis or respiratory endpoints health including premature mortality [21]–[26]. Air pollution affects mostly children and seniors. Aphekom [27] reports that living in close vicinity to busy roads is responsible for approximately 15–30% of all new cases of asthma in children; and of chronic obstructive pulmonary disease and coronary heart disease in adults 65 years of age and older. With the increased awareness of traffic as a major source of diffuse metal emission the need for clear characterization of road deposited sediment becomes more apparent.

The main objective of the study was to analyze road dust sediment as an indicator in the process of assessing and identifying vehicle-derived metal pollution as well as to evaluate the contamination with well-known traffic indicators such as Cr, Cu, Pb, and Zn in road dust obtained from Krakow.

Krakow is one of the most congested cities in Poland. Air quality conditions in Krakow is poor and even in spite of a dramatic decrease in anthropogenic emissions, air pollution of major pollutants within many urban locations have not changed over the span of two decades. In Poland, old cars dominate and the average age of car in Poland is about 15 years. Over span of last two decades the number of vehicles in Poland has increased threefold.

Chemical analysis was additionally supplemented by the fractionation study, since information on the total concentration of metals is not sufficient to assess their potential bioavailability and mobility, as these parameters largely depend on their chemical forms and transport phases. Metals accumulate in the finest fraction mainly constructed of clay mineral, Mn and Fe hydroxides and oxides, carbonates as well as organic matter. Fractionation using BCR protocol is a useful tool to deliver very important information on the issue of mobility, bioavailability of metals, transport mechanisms and consequently the influence of metals on the environment and human health.

2 MATERIALS AND METHODS

2.1 Sampling area

Krakow as the one of the most traffic congested cities of Poland was selected as research site. Sampling points were located as far as possible from industrial plants and, far from residential areas to minimize the impact of contamination sources. Samples were taken monthly starting from March to September 2015. Samples of road dust, including field duplicates, were swept after wetting with a brush from the road (rectangle 2 m x 2 m). Research areas are depicted in Fig. 1 and in Table 1.

2.2 Methods

Road dust samples were digested using *aqua regia* in microwave oven according to protocol 3050B [28]. Total concentration of trace elements (Cr, Zn, Pb and Cu) content was determined by inductively coupled plasma-mass spectrometry (ICP-MS) (ELAN 6100; Perkin Elmer) according to US EPA method 6020A [29]. In order to obtain unambiguous

3th May Av. | Błonia Meadow | Focha St., Błonia Meadow

Figure 1: Błonia Meadow: sampling areas.

Table 1: Sampling area: Błonia Meadow – 3th May Avenue.

SAMPLING POINT LOCATION – KRAKOW GEOGRAPHICAL COORDINATES	
SITES NEAR ROADS WITH HEAVY TRAFFIC AND CONGESTIONS	
Focha St. – 3th May Av. (junction)	50°03’33.2”N 19°55’26.0”E
3th May Av. – Oleandry St. (junction)	50°03’35.1”N 19°55’14.4”E
3th May Av. – Reymana St. (junction)	50°03’40.0”N 19°54’43.5”E
Chodoweckiego St. – 3th May Av. (junction)	50°03’44.6”N 19°54’13.7”E
Piastowska St. – 3th May Av. (junction)	50°03’45.3”N 19°54’09.0”E
Korzeniowskiego – Piastowska St. (junction)	50°03’39.2”N 19°54’04.3”E
Piastowska (bridge)	50°03’36.2”N 19°54’02.0”E
Focha (bridge)	50°03’24.7”N 19°54’24.5”E
Kasztelańska St. – Focha St. (junction)	50°03’27.4”N 19°54’47.9”E
Kraszewskiego St. – Focha St. (junction)	50°03’29.9”N 19°55’04.9”E
Kałuży St. – Focha St. (junction)	50°03’32.0”N 19°55’20.8”E
SITE UNPOLLUTED WITH TRAFFIC	
Korzeniowskiego (garden parcels)	50°03’41.3”N 19°53’57.0”E

and unbiased ICP-MS results, the above-mentioned metals were additionally measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (OPTIMA 7300DV; Perkin Elmer). In order to estimate the accuracy and bias of the analytical method used in the study, reagents blanks and Quality Control Materials: METERNAL^{TM}32 and BCR 701 were used to assure that analytical results meet the required criteria.

Fractionation study was conducted on 3 preselected samples according to BCR protocol [30]. Table 2 presents reagents and environmental conditions for this study.

Statistical parameters of Cr, Zn, Pb and Cu in various grain size fraction of road dust samples are presented in Table 3.

Moreover, statistical parameters of reference samples collected from sites unpolluted by traffic were compiled in Table 4 in order to differentiate between heavy metals derived from vehicles and other sources of contamination.

Table 2: Sequential extraction procedure according to BCR protocol [30], [31].

Step	Fraction	Targets phases	BCR protocol
1	Exchangeable, water and acid soluble	Soluble species, carbonates, cation exchangeable sites	0.11 mol/L acetic acid
2	Rediucible	Fe and Mn oxyhydroxides	0.1 mol/L hydroxylammonium chloride, pH 2
3	Oxidisable	Organic matter and sulphides	Hydrogen peroxide followed by 1.0mol/L ammonium acetate, pH 2
4*	Residual	Remaining, non-silicate bound metals	*Aqua regia* digestion

* The residual extraction step is not included in original procedure but it can be useful for quality control, since sum of steps 1-4 can be compared with digestion protocol 3050B [28], [32].

Table 3: Concentration of traffic related elements in examined road dust.

Road dust (n=11)					
Fraction size Elements (mg/kg)	<20 µm	20–63 µm	63–200 µm	200–1000 µm	1000–2000 µm
Cr (range) (mean)	229–380 276	90.6–279 179	61.6–136 98.3	78.2–152 102	89.1–209 110
Zn (range) (mean)	589–1980 1340	390–1020 648	434–1264 670	257–614 504	189–882 670
Pb (range) (mean)	188–560 356	197–352 247	148–241 204	84.9–378 189	88.0–202 144
Cu (range) (mean)	290–890 439	129–966 304	156–267 198	68.3–212 202	78.2–119 98.1

Table 4: Statistical parameters of reference samples unpolluted with traffic.

Road dust (n=1)					
Fraction size Elements (mg/kg)	<20 µm	20–63 µm	63–200 µm	200–1000 µm	1000–2000 µm
Cr	64.7	56.8	39.8	42.2	39.9
Zn	343	289	197	201	232
Pb	103	76.2	45.3	34.7	50.6
Cu	186	112	98.2	65.2	67.7

It was concluded that road dust collected from traffic polluted sites were significantly (about 5 time more) contaminated then samples collected from the reference sites.

Three samples of road dust were selected for fractionation studies. Results of mobility and bioavailability of metals in the fractions are presented in Fig. 2.

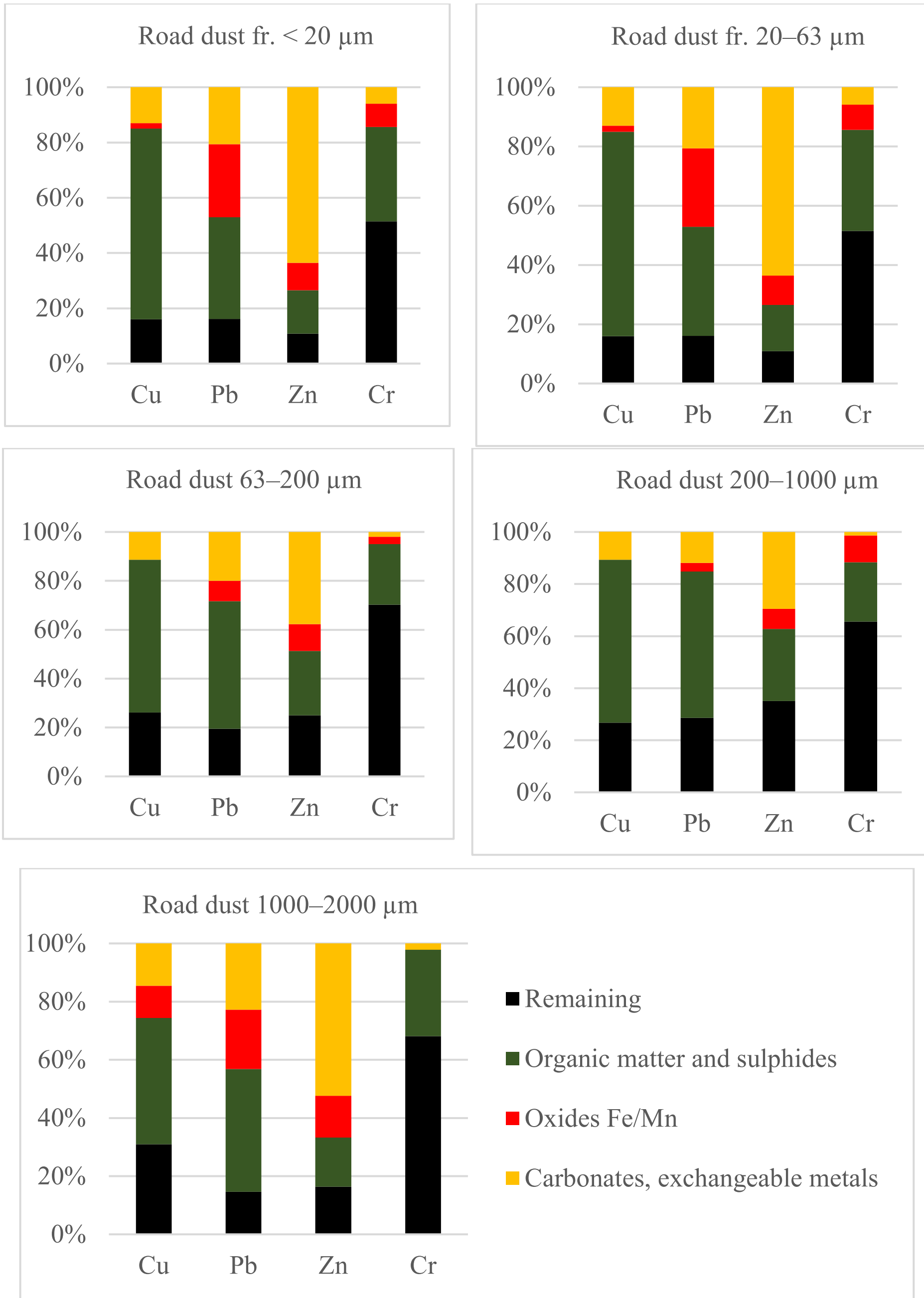

Figure 2: Chemical fractionation of Cu, Pb, Zn and Cr in various grain size of road dust.

Fractionations studies conducted on the selected samples revealed that Zn was the most mobile and bioavailable of all investigated metals, on average 29 to 64% of Zn was bonded with carbonates and/or exchangeable metal fractions. This heavy metal was also the most abundant and was sourced mostly from tire wear. Its high concentrations resulted from the addition of ZnO and ZnS to the tire during vulcanization. Additional significant mobility in the road environment samples was found for Pb, which was up to 29% with easily leachable carbonates and exchangeable fractions. This specific metal can be a cause of extreme threat to the environment. In case of Cu up to 16% was bound with carbonates and/or exchangeable metal fractions. No significant environmental risk was associated with respect to Cr, however when ingested by human all elements could be extremely toxic and even lethal. As estimated by Zhou et al. [33] the exposure dose of Pb, Cd, Cu sourced from road dust by ingestion is two orders of magnitude higher than the corresponding dermal dose and up to four orders of magnitude higher than the inhalation exposure.

3 CONCLUSIONS

Road dust samples collected from traffic polluted sites were significantly more contaminated than samples collected from the reference sites and it can be assumed that the following metals Cr, Zn, Pb and Cu can pose a significant hazard to the environment.

Contamination with zinc can be attributed to the wear and tear of tires, since ZnO and ZnS are added to activate vulcanization in the tire tread as well as it can also be sourced from traffic signals or guardrails [34]. Copper source of contamination is the friction additive in the form of CuS used in a brake system. Lead is an important component of bearing alloys. Until recently lead was used also as a main material for wheel balancing weights but currently it is replaced with zinc weights. It should be however noted that Pb is very persistent element and its elevated concentration in road dust is a consequence of common use of lead in form of organic alkyl lead [35] as gasoline additive in Poland up to March 2005.Contamination of road dust with chromium is a result of adding it as a main component of alloys used to produce wrist pins and connecting rods.

Fractionations studies revealed that Zn was the most mobile and bioavailable of all investigated metals. Additional significant mobility in the road environment samples was found for Pb, which was associated with easily leachable carbonates and exchangeable fractions. No significant environmental risk was associated with respect to Cu

The fraction up to <20 μm of the road dust should be considered a heavy metal pollution indicator since over 90% of break dust is comprised of fine fraction [36], [37], but the same time attention should be drawn to the fact that the significant sources of metals in this fraction of road dust could be of geogenic origin.

Monitoring of fine fraction of road dust should be of special concern since this fraction easily enters into an environment and goes into contact with people. Hazards of traffic related elements in road dust contamination can cause acute and chronic adverse effects on human health. Substantial amounts of road dust (up to 50%) could also be resuspended, in particular on traffic lights, where more braking is involved. On junctions and in close vicinity to traffic lights there are more pedestrians. They are affected by the dust and suffer from the exposure. Such processes as resuspension of road dust as well as exhausted and non-exhausted car emission affect mostly children or babies in strollers since they occur on low ground level. It should be noted that metals in the environment (even when not mobile) can become a serious health concern when ingested or inhaled. Further study on the impact of traffic related emission on human health to evaluate Health Risk Assessment (HRA) should be however of primary interest.

ACKNOWLEDGEMENT

The research leading to these results has received funding from the Polish-Norwegian Research Programme operated by the National Centre for Research and Development under the Norwegian Financial Mechanism 2009–2014 in the frame of Project Contract No. Pol-Nor/208849/106/2015.

REFERENCES

[1] Peters, A., von Klot, S., Heier, M., Trentinaglia, I., Hörmann, A., Wichmann, H.E. & Löwel, H. Exposure to traffic and the onset of myocardial infarction. *The New England Journal of Medicine*, **351**, pp. 1721–1730, 2004.

[2] Riediker, M., Cascio, W.E., Griggs, T.R., Herbst, M.C., Bromberg, P.A., Neas, L., Williams, R.W. & Devlin, R.B. Particulate matter exposure in cars is associated with cardiovascular effects in healthy, young men. *American Journal of Respiratory and Critical Care Medicine*, **169**, pp. 934–940, 2004.

[3] Schwartz, J., Litonjua, A., Suh, H., Verrier, M., Zanobetti, A., Syring, M., Nearing, B., Verrier, R., Stone, P., MacCallum, G., Speizer, F.E. & Gold, D.R. Traffic related pollution and heart rate variability in a panel of elderly subjects. *Thorax*, **60**, pp. 455–461, 2006.

[4] Gerlofs-Nijland, M.E., Dormans, J.A., Bloemen, H.J.T., Leseman, D.L.C., Boere A.J.F., Kelly, F.J., Mudway, I.S., Jimenez, A.A., Donaldson, K., Guastadisegni, C., Janssen, N.A.H., Brunekreef, B., Sandström, T., van Bree, L. & Cassee, F.R. Toxicity of coarse and fine particulate matter from sites with contrasting traffic profiles. *Inhalation Toxicology*, **19**, pp. 1055–1069, 2007.

[5] Maynard, D., Coull, B.A., Gryparis, A. & Schwartz, J. Mortality risk associated with short-term exposure to traffic particles and sulfates. *Environmental Health Perspectives*, **115**(5), pp. 751–755, 2007.

[6] Riediker, M. Cardiovascular effects of fine particulate matter components in highway patrol officers. Inhalation Toxicology, 19(suppl. 1), pp. 99–105, 2007.

[7] Latzin, P., Röösli, M., Huss, A., Kuehni, C.E. & Frey, U. Air pollution during pregnancy and lung function in newborns: A birth cohort study. *European Respiratory Journal*, **33**(3), pp. 594–603, 2009.

[8] Kelly, F.J. & Fussell, J.C. Air pollution and airway disease. *Clinical and Experimental Allergy*, **41**(8), pp. 1059–1071, 2011.

[9] Jedrychowski, W.A., Perera, F.P., Spengler, J.D., Mróz, E., Stigter, L., Flak, E., et al. Intrauterine exposure to fine particulate matter as a risk factor for increased susceptibility to acute bronchopulmonary infections in early childhood. *International Journal of Hygiene and Environmental Health*, **216**(4), pp. 395–401, 2013.

[10] Künzli, N., Jerrett, M., Mack, W.J., Beckerman, B., La Bree, L., Gilliland, F., et al. Ambient air pollution and atherosclerosis in Los Angeles. *Environmental Health Perspectives*, **113**(2), pp. 201–206, 2005.

[11] Hoffmann, B., Moebus, S., Möhlenkamp, S., Stang, A., Lehmann, N., Dragano, N., et al. Residential exposure to traffic is associated with coronary atherosclerosis. *Circulation*, **116**(5), pp. 489–496, 2007.

[12] Bauer, M., Moebus, S., Möhlenkamp, S., Dragano, N., Nonnemacher, M., Fuchsluger, M., et al. Urban particulate matter air pollution is associated with subclinical atherosclerosis. Results from the HNR (Heinz Nixdorf Recall) Study. *Journal of the American College of Cardiology*, **56**(22), pp. 1803–1808, 2010.

[13] Peng, R.D., Chang, H.H., Bell M.L., McDermott A., Zeger S.L., Samet J.M., et al. Coarse particulate matter air pollution and hospital admissions for cardiovascular and

respiratory diseases among Medicare patients. *Journal of the American Medical Association*, **299**(18), pp. 2172–2179, 2008.
[14] Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M., Armstrong, B. Urban ambient particle metrics and health: A time-series analysis. *Epidemiology*, **21**(4), pp. 501–511, 2010.
[15] Mann, J.K., Balme, J.R., Bruckner, T.A., Mortimer, K.M., Margolis, H.G., Pratt, B., et al. Short-term effects of air pollution on wheeze in asthmatic children in Fresno, California. *Environmental Health Perspectives*, **118**(10), pp. 1497–1502, 2010.
[16] Meister, K., Johansson, C., Forsberg, B. Estimated short-term effects of coarse particles on daily mortality in Stockholm, Sweden. *Environmental Health Perspectives*, **120**(3), pp. 431–436, 2012.
[17] Qiu, H., Yu, I.T., Tian, L., Wang, X., Tse, L.A., Tam, W., et al. Effects of coarse particulate matter on emergency hospital admissions for respiratory diseases: A time-series analysis in Hong Kong. *Environmental Health Perspectives*, **120**(4), 572–576, 2012.
[18] Loeb, L.A. A mutator phenotype in cancer. *Cancer Research*, **61**(8), pp. 3230–3239, 2001.
[19] Pope, A.C. & Dockery, D.W. Health effects of fine particulate air pollution: Lines that connect. *Journal of the Air & Waste Management Association*, **56**(6), pp. 709–742, 2006. DOI: 10.1080/10473289.2006.10464485.
[20] Potgieter-Vermaak, S., Rotondo, G., Novakovic, V., et al. Component-specific toxic concerns of the inhalable fraction of urban road dust. *Environmental Geochemistry and Health*, **34**, pp. 689–696, 2012.
[21] van der Gon, H.A., Gerlofs-Nijland, M.E., Gehrig, R., Gustafsson, M., Janssen, N., Harrison, R.M., et al. The policy relevance of wear emissions from road transport, now and in the future—an international workshop report and consensus statement. *Journal of the Air and Waste Management Association*, **63**(2), pp. 136–149, 2013.
[22] Peng, R.D., Chang, H.H., Bell, M.L., McDermott, A., Zeger, S.L., Samet J.M., et al. Coarse particulate matter air pollution and hospital admissions for cardiovascular and respiratory diseases among Medicare patients. *Journal of the American Medical Association*, **299**(18), pp. 2172–2179, 2008.
[23] Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M. & Armstrong, B. Urban ambient particle metrics and health: A time-series analysis. *Epidemiology*, **21**(4), pp. 501–511, 2010.
[24] Mann, J.K., Balme, J.R., Bruckner, T.A., Mortimer, K.M., Margolis, H.G., Pratt, B., et al. Short-term effects of air pollution on wheeze in asthmatic children in Fresno, California. *Environmental Health Perspectives*, **118**(10), pp. 1497–1502, 2010.
[25] Meister, K., Johansson, C. & Forsberg, B. Estimated short-term effects of coarse particles on daily mortality in Stockholm, Sweden. *Environmental Health Perspectives*, **120**(3), pp. 431–436, 2012.
[26] Qiu, H., Yu, I.T., Tian, L., Wang, X., Tse, L.A., Tam, W., et al. Effects of coarse particulate matter on emergency hospital admissions for respiratory diseases: A time-series analysis in Hong Kong. *Environmental Health Perspectives*, **120**(4), pp. 572–576, 2012.
[27] Aphekom. Improving knowledge and communication for decision making on air pollution and health in Europe. *Summary report of the Aphekom project 2008–2011*. www.endseurope.com/docs/110302b.pdf. Accessed 10 December 2016.

[28] EPA. Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. www.epa.gov/sites/production/files/2015-06/documents/epa-3050b.pdf. Accessed 25 May 2017.
[29] EPA. Method 6020A: Inductively Coupled Plasma-Mass Spectrometry. www.epa.gov/sites/production/files/2015-07/documents/epa-6020a.pdf. Accessed 25 May 2017.
[30] Ure, A.M., Quevauviller, P., Muntau, H. &Griepink B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry*, **51**, pp. 135–151, 1993.
[31] Adamiec, E. Chemical fractionation and mobility of traffic related elements in road environments, 2017, in press.
[32] Mossop, K.F. & Davidson, C.M. Comparison of original and modified BCR sequential extraction procedures for fractionation of cooper, iron, lead, manganese and zinc in soils and sediments. *Analytic Chimica Acta*, **478**, pp. 111–118, 2003.
[33] Zhou, Q., Zheng, N., Liu, J., Wang, Y., Sun, Ch., Liu, Q., Wang, H. & Hang, J. Residents health risk of Pb, Cd and Cu exposure to street dust based on different particle sizes around zinc smelting plant northeast of China. *Environmental Geochemistry and Health*, **37**, pp. 207–220, 2015.
[34] Carrero, J.A., Goienaga, N., Olivares, M., Martinez-Arkarazo, I. & Arana, G. Raman spectroscopy assisted with XRF and chemical simulation to assess the synergic impacts of guardrails and traffic pollutants on urban soils. *Journal of Raman Spectroscopy*, **43**(10), pp. 1498–1503, 2012.
[35] Poperechna, N. & Heumann, K.G. Species-specific GC/ICP-IDMS for trimethyl lead determinations in biological and environmental samples. *Analytical Chemistry*, **77**(2), pp. 511–516, 2005.
[36] Grigoratos, T. & Martini, G. Brake emissions: review. *Environmental Science and Pollution Research*, **22**, pp. 2491–2504, 2015.
[37] Adamiec, E., Jarosz-Krzemińska, E. & Wieszała, R. Heavy metals from non-exhaust vehicle emissions in urban and motorway road dusts. *Environmental Monitoring and Assessment*, **188**, p. 369, 2016.