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ASSESSMENT OF THE ROAD TRAFFIC IMPACT ON ACCUMULATION OF SELECTED ELEMENTS IN SOILS DEVELOPED ON KRYNICA AND BYSTRICA SUBUNIT (MAGURA NAPPE, POLISH OUTER CARPATHIANS)

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Abstract: The investigations aimed at assessing an impact of road traffic on the presence and the variability of Zn, Pb, Cr, As, Ti and Ni in soils of a protected area, i.e., the Poprad Landscape Park (Magura Nappe, Outher Carpathian). Soils collected represented three sets: basic samples, control samples and samples expected to be under the highest anthropopression. The assessment was based on determinations of the pH and the genetic type of soils, their total contents of the metals mentioned, and the forms in which cations are bound in the soils. Statistic parameters of these data (coefficients of variability and accumulation) formed the basis to identify the areas of the highest and lowest impact of road traffic on soils. The soils most affected are located in the 5-m wide belt next to the road margin. They reveal a significant change of soil pH and an increase of concentration of metals, mainly of Cd, Pb and Zn, in comparison to the geochemical background determined for the study area. Also the fraction of metals bound in the easily soluble forms is significantly higher in the soils adjacent to the road than that in the soils of the control set (samples of the lowest contamination); it is particularly expressed for Zn, Pb and Cd.

Keywords: landscape park, Magura Nappe, soils, Zn, Pb, Cr, Cd, As, Ti, Ni, road traffic**.**

1. INTRODUCTION

The areas under legal protection require a meticulous, continuous monitoring because of their special character (natural and cultural values) (Blake & Goulding, 2002; Huber et al., 2008; Kibblewhite et al., 2008). Natural resources, particularly those of the animate nature, may deteriorate as a result of wrong management and, in extreme cases, may become significantly impoverished (Abrahams, 2002; Jarup, 2003). The areas and sites with the highest protection status, particularly those important due to UE or international regulations, are usually administered by dedicated agencies, which conduct a whole range of statutory actions aimed at proper securing and functioning of protected ecosystems. The situation is slightly different in the case of large-surface areas, whose natural rank is lower in comparison with national parks, nature reserves, or Man & Biosfere reserves.

Comparing in the world scale the value of protected areas is difficult considering the differences in their national classifications. Using definitions of protected areas of various ranks ($I_{a\text{-}b}$–VI) established by the International Union for Conservation of Nature (IUCN), a protected area being in the Polish legal system a landscape park, which – as such – fulfils criteria of the I_b, III, V and VI IUCN categories, has been selected. It is the area whose geological structure, natural reserves of the plant and animal kingdoms, and cultural values are much diversified. It is also characterized by considerable problems in conducting effective policy of environment protecting; it's enforcing, and implementing the principles of the sustainable development. Within landscape parks even industrial economy can coexist with sites being under strict protection, e.g., nature reserves and monuments, or the Nature 2000 areas (Nelson et al., 1993). The landscape parks are normal, inhabited, rural and/or suburban and/or urban areas, intersected by a network of roads along which motor vehicles transporting people, animals and goods move (Adriano et al., 1997; Kicińska-Świderska et al., 2005; Massas et al., 2013; Modrzejewska & Wyszkowski, 2014). These vehicles emit various substances (e.g., As, Cd, Cr, Ni, Pb, Ti, Zn) polluting the soil-plant environment, and in a consequence decreasing the overall environment quality, while in extreme cases excluding from the agricultural use the land zones adjacent directly to the roads (Haiyan & Stuanes, 2003; Imperato et al., 2003; Lin & Yu, 2008; Balaban et al., 2011; Zhang et al., 2012). The metals accumulating in soils may penetrate the plant cover in substantial amounts, in this way introducing contaminants into the trophic chain (Jarup, 2003; Kabata-Pendias & Mukherjee, 2007; Grobelak et al., 2013).

2. STUDY AREA

An assessment of the road traffic impact on soils located in closer and distant neighborhoods of transportation tracts was carried out in the Sądecki Beskid Mts, which belong to the arc of the Outer Carpathians (Flysch Carpathians) and are almost as a whole protected as the Poprad Landscape Park and a Natura 2000 area (Kicińska, 2012*a*). The wealth of their nature is marked by the occurrence of 14 nature reserves, 75 monuments of the animate nature and 26 monuments of the inanimate nature, including 12 legally protected springs of mineral waters. Balneological resources are widespread within the area and they have formed the bases of many tourist centers and also five, renowned in Europe health resorts being the statutory spas (Fig. 1).

An annual number of visitors are impressive: it exceeds 270,000, they spent there 1.5 mln person-nights (GUS, 2012). Specialized leisure time activities include mountain tourism, cycling, alpine or cross-country skiing, some people also come for health reasons.

The study area has the highest biocenter rank in the ECONET-POLAND classification (European ECOlogical NETwork), it is a nature core area with an international significance and occupies around 550 km^2. The area is intersected by a network of national and local roads, whose density in 2010 was 0.32 km/km^2; the length of district roads in 2010 was 2.45 km per 1000 inhabitants (GUS, 2012). The number of residents is around 240,000, out of which 48% live in towns and the remaining 52% in the countryside. The average population density is 130 persons per 1 km^2 (GUS, 2012).

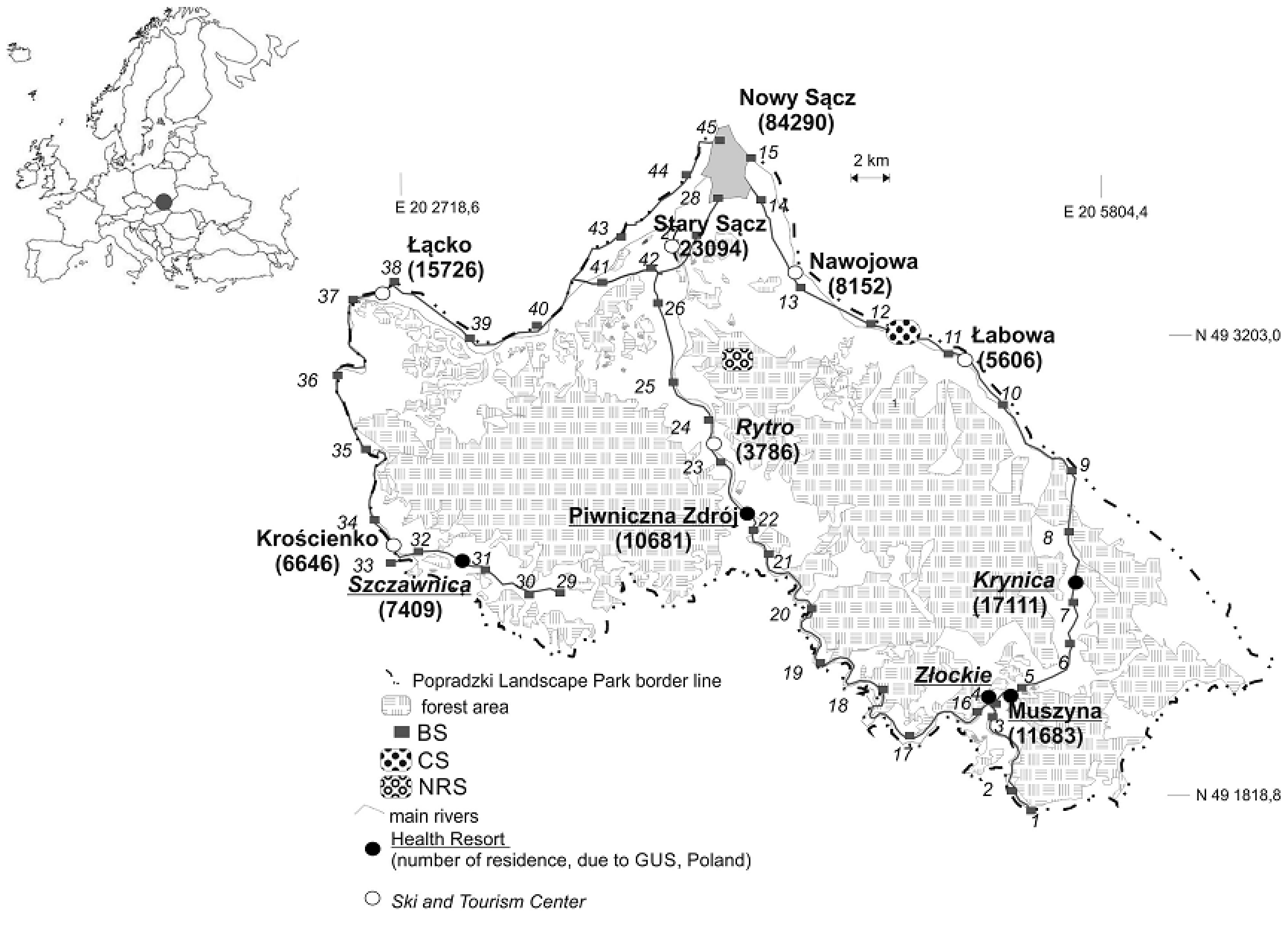

Figure 1. Location of the sampling sites

3. MATERIALS AND METHODS

The soils of the Sądecki Beskid Mts have been developed as a result of combined processes that took place on a rocky bedrock composed of flysch strata (Kicińska, 2012*a*). The surface soil samples represent a depth layer of 0-20 cm and were collected as channel samples according to the standards PN-ISO 11074-1:2001P and PN-ISO 11074-2:2001P. The investigations were carried out along three selected roads spanning major urban, tourist and spa centers. In order to establish the variability of metal distribution in soils and the impact of road traffic on the soils, three different sample sets were collected: a) Basic Set (BS); it represents the soils from the whole study area, affected by road traffic of various intensity; b) Near-Road Set (NRS), the set of 30 samples (*n=30)* collected along a road with intensive traffic; the samples were taken at each 1 m along the road margin. This set represents soils affected by fuel combustion and resulting gas emissions along a short, 30-m long road section; c) Control Set (CS) of 30 samples (*n=30*), composed of soil samples not being under traffic pressure (not any road close to the sampling site) and collected in the nods of a 1x1 m grid. This set is characteristic of an area with lowest anthropopression, and the impact of road traffic is close to nil.

The basic set BS is composed of the soil material collected in 45 sites approximately 5 km distant from each other and distributed along major road tracts with a total length of 156 km (Fig. 1, samples numbered 1-45); the samples were taken at 0.5 m outside the road edge. These major road tracts were divided into three sections, designated T1, T2 and T3.

The section T1 (53 km long) is a fragment of the national road no. 75 that joins Nowy Sącz (the capital and simultaneously the largest town of the Sądecki Beskid region) with Leluchów, a border crossing with Slovakia (sampling sites number 1–15, Fig. 1).

The section T2 (46 km long) is a fragment of the national road no. 87 that joins a spa resort of Muszyna with towns Stary Sącz and next Nowy Sącz (sampling sites numbered 16–28, Fig. 1);

The section T3 (57 km long) is a fragment of the local road no. 969 that joins two touristic localities, Jaworki and Biała Woda in the Little Pieniny Mts with Nowy Sącz (sampling sites numbered 29–45, Fig. 1).

In order to analyse in the BS the local geochemical variability in relation to the regional geochemical variability, replicate samples were collected in each forth site (Fig. 1, sampling sites numbered 2, 6, 10, 14, 17, 21, 25, 30, 34, 38 and 43) and in further processing treated according to the same chemical procedures (decomposition and assays) as the samples of the basic set. Evaluations of the statistical variability and of the precision of analysing and sampling were carried out with the variance analysis ANOVA, which determines the impact of individual factors on a variability development (Ramsey, 1992; Yay et al., 2008). The geochemical and technical variances (the latter being a total of the analytical variance and sampling variance) were calculated with the ROBOCOOP3 software (at the amount of replicate samples not lower than 11). The Statistica10 software was used to calculate correlation coefficients.

In order to determine the dependence between the variability of concentration of selected elements and the distance from the road edge, in six sites of the BS (Fig. 1, sampling sites numbered: 2, 15, 16, 28, 29 and 45) the samples were collected in the distances 0.5, 5.0 and 50 m from the road edge; they were named distant samples.

Chemical determinations were conducted using a sequential extraction as it makes possible the identification of binding forms of metals in soils and, thus, of a potential threat to the environment. The forms of binding control the mobility of an element, its bioavailability and possible ecosystem hazards (Tokalioglu et al., 2003; Viard et al., 2004; Noori et al., 2010; Van Beek et al., 2010).

The soil samples were dried at a temperature of 105^{o}C and decomposed according to the EPA-3051 standard (65% HNO_3 + 30% H_2O_2) in three pressure ranges (90, 100, 110 psi) in a microwave oven. The sequential extracting was carried out in four stages using the BCR procedure (Quevauviller et al., 1998), i.e., applying a sequence of the following reagents and pH conditions:

- Stage 1 - F1 - acid extractable fraction - 0.1 M CH_3COOH (pH=3),
- Stage 2 - F2 - reducible fraction - 0.1 M $NH_2OH{\cdot}HCl$ (pH=2),
- Stage 3 - F3 - oxidisable fraction - 30% H_2O_2+1M CH_3COONH_4 (pH=2),
- Stage 4 - F4 - residual fraction - 65% NHO_3.

This procedure makes possible determination of the types and contents of respective metals: F1 - easily soluble in an acid environment, F2 - prone to reducing, F3 - prone to oxidizing, and F4 - left behind as a residuum. The concentrations of Zn, Pb, Cr, Cd, As, Ti and Ni in solutions were assayed using an ICP-MS Elan 6100 Perkin Elmer instrument (detection limit $2{\cdot}10^{-5}$ mg·dm^{-3}).

4. RESULTS AND DISCUSSION

The variance analysis indicate that the proviso of the calculated technical variance contribution to the total variance of not being higher than 20% has been fulfilled in case of all the metals analysed for, which allows drawing geochemical conclusions and is a proof of the so-called analytical reliability of the methods applied.

The soils studied belong to autogenic soils in their taxonomic classification. Among them the brown soils prevail with a typical Ap-Bbr-BCgg development of the profile, in which transition horizons A/Bbr and Bbr/Cca may occur in places. The Ap horizon is usually fifteen or so centimeters thick, medium moist, and contains various amounts of sandstone rubble. The next in profile horizon (Bbr) is brownish and represents the medium granular loam containing significantly more sandstone rubble (up to 45–50%) than the previous layer. Going down, the amount of the coarse-grained sandstone rubble (sandstone debris) increases even to 90%, and the soil is a typical light granular loam. Other soil types established represent lithogenic, semi-hydrogenic and hydrogenic soils accompanied by alluvial soils (alluvia *sensu stricto* and brown deluvial soils). The samples studied belong to proper brown soils.

4.1. pH

The range of the pH_{H2O} values of the soils oscillates between 4.8 and 8.1, which indicates that the soils studied belong to all pH soil types: strongly acid, acid, weakly acid, neutral and basic (Kicińska, 2012*b*). Considering the three soil sets separately, the pH values are significantly diversified. The range of pH values measured in the BS soils is 5.8–7.7 and shows the normal distribution. Their average pH (*A*) is 6.9 and the pH range 6.7–7.4, but as high as 75% (distinct prevalence) of the soils reveal the neutral reaction. There are no strongly acid soils within the BS. The pH values within the CS and NRS have also the normal distributions but occurring in considerably different pH ranges. The soils of the NRS have revealed the highest pH values (7.6–8.1, *A*=7.8), which points to their dominant basic reaction. On the contrary, the CS soils that are under the lowest anthropopression have their reactions typical of strongly acid or acid soils (pH ranges from 4.8 to 5.5, *A*=5.2).

When comparing the pH values of soils of the three sets, it is seen that the values in the BS and NRS are similar, but strongly differ from those belonging to the CS (Fig. 2). Assuming that the pH determined in the CS is a value of the geochemical background of the soils within the study area, pollution by road vehicles in the other two sets significantly affects the soil pH values and increases them by around 1.7 pH units.

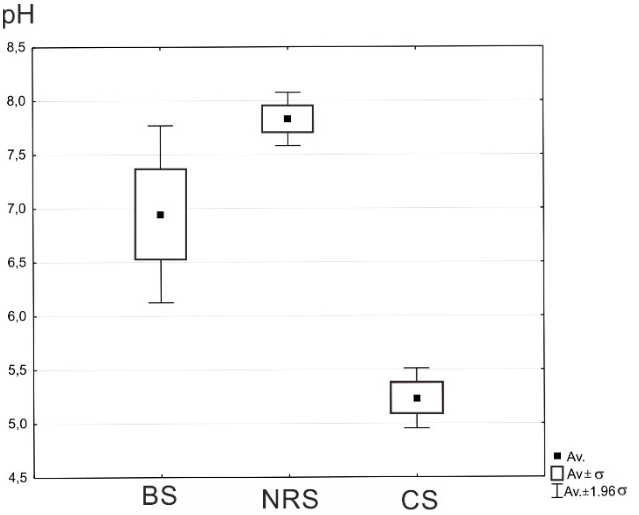

Figure 2. Ranges of pH values in the sampling sets

The calculated variability coefficient *V* (*V*=a quotient of the standard deviation and arithmetic mean) is the highest (*V*=0.06) for the BS, the lowest (*V*=0.02) for the NRS; the coefficient of the CS has an intermediate *V* value of 0.03. The coefficient indicates a uniform impact of contaminants on soils along the NRS section (samples collected at each 1m), and the impact of factors controlling pH of soils of the CS samples as also uniform, however in the latter case these are natural factors.

With regard to the pH values, the soils of the BS are the least uniform, while those of the NRS are the most uniform.

4.2. Contents of selected metals in soils

The content ranges of the selected elements were compared to the natural contents (NC) characteristic of sandy soils (Kabata-Pendias & Szteke, 2012). In the case of As, Cr, Ni and Ti, 90% of the soil samples from the BS and NRS do not exceed the NC values (Table 1).

However, almost half of the BS samples and about 10% of the NRS samples have their Pb contents exceeding the upper NC value, i.e., $40 mg\cdot kg^{-1}$; in all samples their Zn contents are significantly higher than the upper NC value 60 $mg\cdot kg^{-1}$ for sandy soils. In the case of Cd as high as 99% of the soils belonging to the BS have their Cd contents above 0.20 $mg\cdot kg^{-1}$. In all samples of the two remaining sets (NRS and CS), the contents of Zn and Cd are higher than the NC values (Kabata-Pendias & Szteke, 2012).

Table 1. Statistical parameters describing the contents (mg·kg^{-1}) of selected elements in soils

element	min.-max.	median (Me)	average	NC[1]	GB[2]	The number of samples (%) exceeding			
						the upper limit NC		the upper limit GB	
						BS[3]	NRS[4]	BS	NRS
As	3–37	5	5	0.1–30	5±1.2	1	0	14	6
Cd	0.1–12.3	0.6	1.3	0.01–0.2	0.6±1.1	100	100	15	3
Cr	18–53	30	31	40	30±5	11	4	24	43
Ni	4–37	17	17	7–33	17±5	6.2	0	22	96
Pb	13–119	39	45	5–40	39±18	47	10	34	43
Ti	36–479	109	161	200–17 000	109±92	0	0	28	57
Zn	65–541	158	176	30-60	158±65	100	100	25	80

[1] NC – Natural Content - the value assumed for sandy soils by Kabata-Pendias & Szteke (2012),

[2] GB – Geochemical Background calculated according to the formula Me+2MAD (median+2 median absolute deviation)

[3] BS – Basic set - number of samples $n=91$,

[4] NRS – Near-road set- number of samples $n=30$,

The results were also compared with the geochemical background (GB) of the respective soil geotype (Table 1). The GB range of elements were calculated according to the formula (Me±2MAD) proposed by Reimann et al. (2005). The following observations have been made:

- in the case of the BS soils, their contents of Cr, Ni and Zn in around 20% samples significantly exceed the upper GB limit; those of As and Cd do it in 14% samples; and those of Pb in 34% samples;
- in the case of the soils collected along a busy road (set NRS) the contents of Cr, Ti and Pb for almost a half of the samples were higher than the calculated upper GB limits of these metals, whereas for Ni and Zn the upper GB limits were exceeded, respectively, by 96 and 80% of the samples.

Comparing the border values of the NC and GB with the data of other authors, the contents of the metals considered in the soil samples selected for calculation of the geochemical background are distinctly:

- lower (significant differences) for As, Ni and Ti,
- comparable for Cr and Pb,
- higher (significant differences) for Cd and Zn; at the same time the lower GB limit is higher than the upper limit of the NC.

The reasons of the elevated Cd and Zn values may result either from higher, natural contents of these two elements in the soil bedrocks, or from deposition of airborne contaminants of a distant origin (Kabata-Pendias & Pendias, 1999; Blake & Goulding, 2002; Prundeanu & Buzgar, 2011). Therefore, to explain a source of high contents of Cd and Zn in the soils analysed, their assays have been compared to the Cd and Zn contents of the Carpathian flysch rocks (Kicińska, 2012*b*). In the sandstones and mudstones, the Cd contents range from 0.3 to 5.4 mg·kg^{-1} (A=0.55 mg·kg^{-1}) and the Zn contents from 9.5 to 68.6 mg·kg^{-1} (A=32 mg·kg^{-1}). Thus, it may be concluded that the contents of Cd in the soils result from higher natural Cd contents of their parent flysch rocks, whereas the amounts of Zn may result from distant emissions transported by distant wind emissions.

Correlation coefficients among the metals selected for the study indicate that in the soil samples Zn and Pb are highly correlated ($r^2=0.72$), the correlation of Cd with Zn is medium ($r^2=0.45$), while the correlation of Cd with Pb is weak ($r^2=0.28$). These results show that Zn and Pb originate from the same source, irrespective of the contents of these two elements in the soils.

4.3. Soil contents of metals

The data obtained for the BS were used in the cluster analysis, which allowed distinguishing two clusters marked as Z_1 and Z_2 in figure 3. The average soil contents of Zn, Pb and Cd were calculated for both clusters and the results have been found to be statistically significant. In the case of the Z_1 cluster, the average Zn content is 272 mg·kg^{-1}, while for the Z_2 set is 143 mg·kg^{-1} (almost half of the former). Similar figures have been obtained in the case of Pb, as its average amount of the Z_1 cluster is approximately twice as high (73 mg·kg^{-1}) as that of the Z_2 cluster (35 mg·kg^{-1}). The average Cd content is higher of the Z_1 cluster (1.17 mg·kg^{-1}) than that of the Z_2 cluster (0.82 mg·kg^{-1}).

Attributing specific localities to the clusters distinguished, it has been established that the Z_1 cluster, the one with higher concentrations of the metals in its soils, encompasses the touristic localities (Muszyna, Krynica, Nawojowa, Piwniczna, Jaworki – Biała Woda, Łącko), attracting visitors not only in the summer but also in the winter. In the Z_2 cluster, in which these concentrations are distinctly lower, encompassed are the areas located among the Z_1 localities mentioned above or those without a large road transport center.

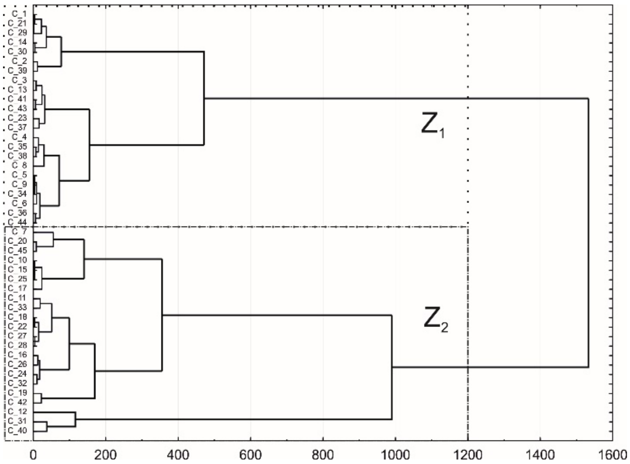

Figure 3. Dendrogram of the basic set (BS)

The most polluted samples are those of soils collected within the limits of the Nowy Sącz town (Zn: 130–316, Pb: 40–83, Cd: 0.5–1.5 mg·kg^{-1}). Significantly lower are the contents of Zn and Cd in smaller localities, such as Leluchów or Muszyna. This result points to on a relation between the degree of soil contamination and an intensity of road traffic.

The next dependence studied, i.e., the content of Zn, Pb and Cd in soil *versus* the distance of the sampling sites (0.5, 5 and 50 m – so-called distant samples) from the road margin. The following regularities have been found for all the distant samples: - the highest contents of the metals occur in the samples situated immediately next to the road margin (Zn 114–316, Pb 36–83 and Cd 0.4–1.5 mg·kg^{-1}); - the lowest contents of the metals occur in the samples most distant from the road margin, - the highest drop in the metal content (about 60% for Zn and Pb, and even 80% for Cd) occurs within the first five meters from the road margin.

Figure 4 shows the linear dependence between Zn and Pb contents and the distance from a road.

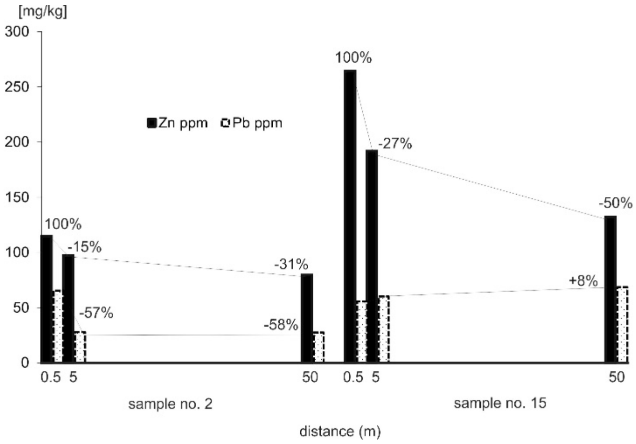

Figure 4. Concentration of Zn and Pb in distant samples (sampling sites 2 and 15, Fig. 1)

4.4. Forms of metal binding

The forms of metal binding were studied in the soil samples with the highest contents of the metals in each of the three sample sets. The most diversified forms of metal binding have been found in the case of Cd, Pb and Zn (Table 2).

The highest amount of Pb, contributing to about 50-90% of the Pb total content irrespective on the degree of soil contamination, is associated with the organic matter and sulphides (F3), the lowest amount (contribution of about 0.6-8%) with the forms easily soluble in the acid environment (F1) and those associated with amorphous oxihydroxides of Fe and Mn (F2). In the residual fraction remains only 10–14% of the total Pb.

There are considerable differences of Zn binding among the samples. In the soils with the lowest anthropogenic impact (CS), more than 60% of the total Zn occurs in the residual fraction, about 27% in the sulphide fraction, 8% is bound in the forms easily soluble in the acid environment and the remaining Zn cations (only about 4%) are prone to reduction (F2). In the soils affected most by road traffic (NRS) the highest portion (47%) of the total Zn is associated with the organic (oxidisable) fraction, 24% with the residual one, about 16% (twice as much as in the CS soils) is easily soluble in the acid environment.

Table 2. Contribution (in % of the total content) of the forms binding metals in soils

Fraction	**Cd**			**Pb**			**Zn**		
	BS	NRS	CS	BS	NRS	CS	BS	NRS	CS
F1 - acid extractable	18	37	61	0.6	6	8	6	16	8
F2 - reducible	13	14	24	0	12	28	4	13	4
F3 - oxidisable	57	38	11	90	70	50	76	47	27
F4 - residual	12	11	4	9.4	12	14	14	24	61

BS – Basic Set, NRS – Near-Road Set, CS – Control Set

In the BS, the highest amount of Zn cations (76%) is bound with the F3 fraction, the least (4%) with the F2 fraction. The Zn binding forms easily soluble in the acid environment represent 6%, while in the residuum remains 14% of the total Zn amount, the lowest value among the three sample sets distinguished.

The most part of total Cd amount from the least affected soils by anthropogenic factors (CS set), as high as 61% of the total content, is easily soluble in the acid environment (F1 fraction). This high contribution can be explained by the highest mobility of Cd in the soils with pH between 4.5 and 5.5, and a similar reaction was determined in the solution from the first step of the sequential extraction. The fraction prone to oxidation makes up only 11% of the total Cd amount, and the residuum binds only 4% of the total Cd. In the two other sample sets (BS and NRS), Cd is bound mainly by sulphides and organic matter, 57 and 38% respectively. Geochemically, Cd shows the highest ability to form compounds with sulphur and those to be bound by Fe hydrooxides and organic matter (Kabata-Pendias & Pendias, 1999). The least amount of Cd is associated with the residuum (about 11% of the total), while about 13% of the total with amorphous hydrooxides of Fe and Mn.

In the case of As, Cr, Ni and Ti, the three sample sets distinguished show comparable speciation among the individual forms of their binding (Fig. 5). Most of the As cations (about 80–90%) are associated with the fraction prone to oxidation, i.e., with organic matter and sulphides, whereas some 10–15% of the total remains in the residuum. The amounts of As bound by amorphous hydrooxides of Fe and Mn do not exceed 4% of the total As, and the As cations in the fraction easily soluble in the acid environment do not represent more than 2% of the total content of this element. The residual fractions contribute most to their total contents makes up as high as 92% of the total Cr and 60-82% of the total Ti. The differences in the contributions of Cr to the F4 fractions (residuum) among the three sample sets are negligible.

The Cr and Ti cations bound by carbonates and/or present at the exchangeable sites (F1 fraction), as well as those combined with amorphous oxyhydroxides of Fe and Mn (F2 fractions) occur practically in traces (<0.01%). The organic matter and sulphides bind in the F3 fraction about 8% of the Cr cations and from 20% (BS) to 40% (CS) of the total Ti amount.

The amounts of Ni easily soluble in the acid environment do not exceed 2% of the total nickel, while up to 8% of Ni in soils is bound by amorphous oxyhydrooxides of Fe and Mn. The organic matter and sulphides bind 22–32% Ni, and in the residuum remains from 65% (BS) to 70% (CS) of the total amount of Ni. The residual fraction contains the metals strongly bound by the mineral components of soils, as in the course of primary and secondary processes these elements have been incorporated in the crystalline structure of minerals and in mineraloids. These amounts of Ni are practically immobilized in insoluble compounds and, thus, unavailable to the plants; for this reason they are not potentially hazardous to the environment.

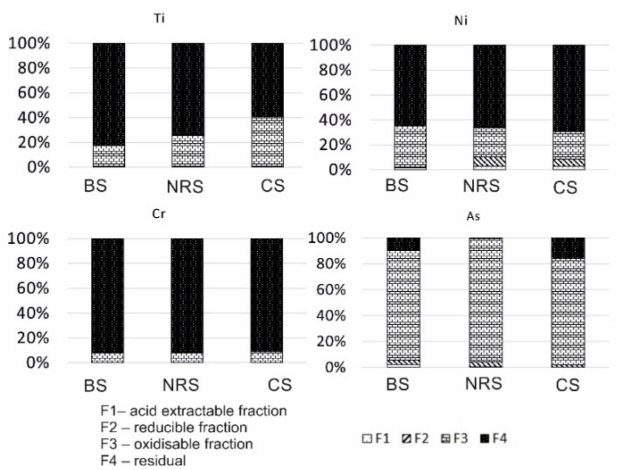

Figure 5. Contributions (% of the total content) of the binding forms of As, Cr, Ni and Ti in soil samples.

5. DETERMINATION OF THE ROAD TRAFFIC IMPACT ON THE SOIL CONTENTS OF METALS

An impact of the road traffic on the soils of a protected area was analysed on the basis of the contents of selected metals. Having obtained the data for three sets of samples, the succession of procedures undertaken and further reasoning (listed below in points 1–4) have been proposed.

1. Comparison of the metal contents in soils of the CS and NRS, providing that the sample dimension of the CS should be not lower than 15 (*n>15*), and that of the NRS should be higher than 30 (*n≥30*).

The data of both sets (Fig. 6) indicate that:

- the ranges of metal contents assayed in the CS samples should be considered the geochemical background characteristic of the soils within the whole study area;
- Zn, Ni, Pb and Cd soil contents of the NRS are 2–3 times higher than those of the CS;
- As, Ti and Cr soil contents of both sets do not reveal significant differences;
- pH soils exposed to contamination by emissions originating from combustion of fuels by road

vehicles is higher in relation to the pH of control soils.

At this stage we must also establish the reliability of assaying expressed by the variability (coefficient *V* calculated as the quotient of the standard deviation and the mean or the median) of the elements assayed for in both sets (CS and NRS). The value of the variability coefficient should be not higher than 0.2. The values higher than that point to significant errors that could arise during sampling, preparing and processing the sample, and/or chemical determinations. If present, such errors make impossible drawing further geochemical conclusions.

2. After having the geochemical background established, two coefficient are analysed for the BS of samples that represent the study area: the accumulation coefficient ***K*** calculated as the quotient of the metal content in the sample and the maximum content of the metal of the geochemical background.

In the case of As, Cr and Ti, the value of ***K*** is lower than 1, which means that the accumulation of these metals in the soils is low. The calculated values of the accumulation coefficient for the remaining metals are higher than 1: Cd *K=2.0*, Zn *K=1.8*, Pb *K=1.5*, and Ni *K=1.3*. The accumulation level of these elements in the soils should be considered as medium.

3. An assessment of the road traffic impact on the soil environment may be too general and not precise enough for such a vast and differentiated area.

Considering the above statement, the cluster analysis has been applied (Fig. 3). On its basis two clusters Z_1 and Z_2 have been distinguished, and accumulation coefficients calculated for both (Tab. 3). As it was in the case of calculated means, the accumulation coefficients for the Z_1 and Z_2 differ, with higher values found in the latter (Z_2). The highest coefficient, *K=3.4*, has been established for Cd, for Zn it equals 2.7, and for Pb 2.2. The accumulation coefficients for the Z_1 cluster are lower than those calculated for the whole BS. These results indicate that the two clusters represent:

- in the case of the Z_1 – the area with a low impact of road traffic,
- in the case of the Z_2 – the area with a medium impact of road traffic.

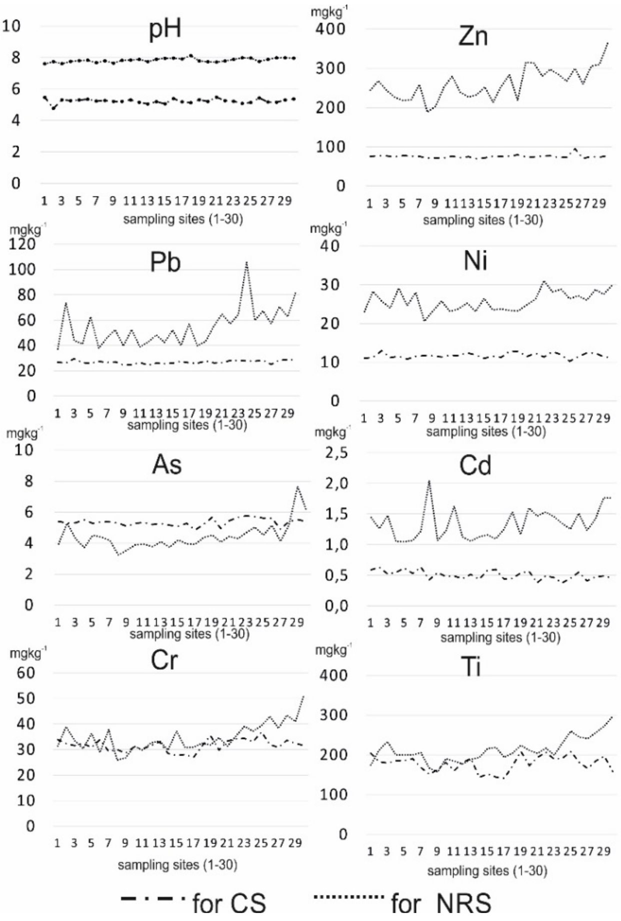

Figure 6. Zn, Ni, Pb, Cr, Cd and Ti in samples collected in the Sądecki Beskid Mts. (data sets NRS and CS)

4. Having the genetic type of the soils identified and considering the framework guidelines for agriculture pertaining to the limits of trace metals in the surface soil layer, the soils in question may be classified regarding their contamination (Kabata-Pendias & Szteke, 2012).
5. As the soils within the study area belong to the classes of light and medium soils, their metal contents show elevated levels and, in some cases, weak contamination; (the levels I and II in the scale used by the Institute of Soil Science and Plant Cultivation (IUNG, Puławy) in Poland 0-VI for Zn, Pb and Cd.

Table 3. Coefficients of variability (*V*) and accumulation (K) of the soils of the protected area (BS)

Parameters		Zn	Pb	Ni	As	Cd	Cr	Ti
V		0.49	0.51	0.40	0.65	1.5	0.22	0.71
K	BS	1.83	1.5	1.32	0.94	2.04	0.84	0.77
	Z_1	1.34	1.06	1.25	0.84	1.48	0.85	0.80
	Z_2	2.74	2.22	1.28	0.89	3.27	0.80	0.90

Z_1 – cluster with a low impact of road traffic
Z_2 – cluster with a medium impact of road traffic

6. CONCLUSIONS

Accumulation of metals in soils depends not only on the type of the parent rock and the grain size distribution of the soil, but also on industrial, agricultural and transportation contaminations. Considering the latter, the author have drawn the following conclusion based on the study results:

1. Road tracts significantly affect the degree of contamination of the land zones in their immediate neighbourhood.
2. The highest hazard of road results from accumulations of Zn, Cd and Pb in soils, with regard not only to the presence of these elements, but also to a significant increase of mineral and organic phases containing easily soluble forms of metal binding.
3. The strongest impact on soils takes place in belts 5 m wide located adjacent to the roads, thus such areas should be unconditionally excluded from any agriculture use, grazing included.
4. Any proper assessment of the impact of a factor degrading the soil environment should include not only basic and control samples but also reference samples that are most sensitive to the factor considered.
5. Geochemical characteristics should be prepared on sufficiently numerous sample sets and based at least on several statistic parameters. Evaluation of the analytical and geochemical reliabilities is also necessary.

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REFERENCES

Abrahams, P.W., 2002. *Soil, their implications to human health*. Science Of The Total Environment. 291, 1-32.

Adriano, D.C., Chen, Z.S., Yang, S.S. & Iskandar, I.K., 1997. *Biogeochemistry of trace metals.* Northwood, Science Reviews. 1–432.

Balaban, S-I., Iancu O.G. & Bulgariu D., 2011. *The geochemical distribution of heavy metals for some mine tailings from the fundu Moldovei area, Romania.* Carpathian Journal of Earth and Environmental Sciences, 6, 2, 279–288.

Blake, L. & Goulding, K.W.T., 2002. *Effect of atmosphere deposition, soil pH and acidification on heavy metal concentration in soils and vegetation of semi-natural ecosystem at Rothamsted experimental station, UK.* Plant and Soil, 240, 235–251.

Grobelak, A., Kacprzak, M., Grosser, A. & Napora, A., 2013. *Chemophytostabilisation of soil contaminated with cadmium, lead and zinc*. Annual Set the Environment Protection, 15, 1982–2002.

GUS- Central statistical Office, *Statistical yearbook of the Republic of Poland*. Warsaw. 1–905.

Haiyan, W. & Stuanes, A.O., 2003. *Heavy metal pollution in air-water-soil-plant system of Zhuzhou City, Hunan Province, China.* Water, Air, And Soil Pollution, 147, 79–107.

Huber, S., Prokop, G., Arrouays, D., Banko, G., Bispo, A., Jones, R.J.A., Kibblewhite, M.G., Lexer, W., Möller, A., Rickson, R.J., Shishkov, T., Stephens, M., Toth, G., Van Den Akker, J.J.H., Varallya, G., Verheijen, F.G.A. & Jones, A.R. (*Eds*)**,** 2008. *Environmental assessment of soil for monitoring, Volume I, indicators and criteria.* Eur. 23490 En/1, Office for official publications of the European communities, Luxembourg, pp. 339.

Imperato, M., Adamo, P., Arienzo, M., Stanzione, D. & Violante, P., 2003. *Spatial distribution of heavy metals in urban soils of Naples City (Italia).* Environmental Pollution. 124, 247–256.

Jarup, L., 2003. *Hazards Of Heavy Metal Contamination*. British Medical Bulletin. 68, 167–182.

Kabata-Pendias, A. & Mukherjee, A.B., 2007. *Trace elements form soil to human*. Berlin, Springer. Pp. 550.

Kabata-Pendias, A. & Pendias, H., 1999. *Biogeochemistry of trace elements.* Warszawa PWN, pp. 398.

Kabata-Pendias, A. & Szteke, B., 2012. *Trace elements in geo- and biosphere*, Puławy. 1–270.

Kibblewhite, M.G., Jones, R.J.A., Baritz, R., Huber, S., Arrouays, D., Micheli, E. & Stephens, M. (*eds*)., 2008. *Environmental assessment of soil for monitoring, Volume VI, Soil monitoring system for Europe*. Eur 23490 En/6, Office For Official Publications Of The European Communities, Luxembourg. 1–88.

Kicińska, A., 2012*a*. *Geochemical diversification of the Beskid Sądecki Mts. And its impact on the transport of selected elements*. Disserations, Monographs 252, AGH- Kraków, pp. 153.

Kicińska, A., 2012*b*. *Spatial variation of pH values of soil developed on the flysch rocks*. Polish Journal of Environmental Studies, 21,5A, 170–174.

Kicińska-Świderska, A., Bazarnik, K. & Kowalska, J., 2005. *The structure of road traffic and lead concentrations in krynica soils.* In: Geotourism – new dimensions in XXI century tourism and chances for future development, 2nd International Conference, Kraków, Poland, 68–69.

Lin, J. & Yu, D., 2008**.** *Traffic-related air quality assessment for open road tolling highway facility.* Journal of Environmental Management, 88, 962–969.

Massas, I., Kalivas, D., Ehaliotis, C., & Gasparatos, D., 2013. *Total and available heavy metal concentrations in soils of the Thriassio plain (Greece) and assessment of soil pollution indexes.* Environmental Monitoring and Assessment,185 (8), 6751–6766.

Modrzejewska, B. & Wyszkowski, M., 2014. *Trace metals content in soils along the state road 51 (Northeastern Poland)*. Environment Monitoring Assessment, 186, 2589–2597.

Nelson, J.G., Butler, R. & Wall, G., 1993. *Tourism and sustainable development, monitoring, planning, managing*. University of Waterloo, pp. 284.

Noori, R., Karbassi, A. & Sabahi, M.S., 2010. *Evaluation of PCA and gamma test techniques on an operation for weekly solid waste prediction*. Journal of Environmental Management, 91, 767–771.

Polish Norms Of Soil Research PN-ISO 11074-1,2001P AND PN-ISO 11074-2,2001P. 1–23 and 1–31.

Quevauviller, P., 1998. *Operationally defined extraction procedures for soil and sediment Analysis I. Standardization*. Trends In Analytical Chemistry, 17, 289–298.

Prundeanu I.M. & Buzgar N., 2011. *The distribution of heavy metals and As in soils of the Falticeni municipality and its surroundings.* Carpathian Journal of Earth and Environmental Sciences, 6, 1, 51-64.

Reimann, C., Filzmoser, P. & Garret, R.G., 2005. *Background and thresholds: critical comparison of methods of determination*. Science of the Total Environment, 346, 1-16.

Ramsey, M.H., Thompson, M. & Hale, M., 1992. *Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance*. Journal Geochemistry Explorer, 44, 23–36.

Regulation of the Minister of the Environment on September 2002 on the standards of the soil quality and ground quality 1.09.2002. Dziennik Ustaw, Nr 165, 1359 (In Polish).

Tokalioglu, S., Kartal, S. & Birol, G., 2003. *Application of three stage sequential extraction procedure for the determination of extractable metal content in highway soils*. Turkish Journal of Chemistry, 27, 333–346.

US-EPA Method 3051, 1994. *Microwave assisted acid digestion of sediment, sludges, soils and oils,* pp. 30.

Van Beek, C.L., Toth, T., Haygo, A., Toth, G., Cala Boix, L., Ano Vidal, C., Malet, J.P., Maquarie, O., Van Den Akker, J.J.H., Van Der Zee, S.E.A.T.M., Verzandvoort, S., Simota, C., Kuikman, P.J. & Oenema, O., 2010. *The need for harmonizing methodologies for assessing soil threats in Europe*. Soil Use And Management, 26, 299–309.

Viard, B., Pihan, F., Promeyarat, S. & Pihan, J.C., 2004. *Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution, bioaccumulation in soil, graminaceaeand land snails*. Chemosphere, 55, 1349–1359.

Yay, O.D., Alahga, O. & Tuncel, G., 2008. *Multivariate statistic to investigate metal contamination in surface soil.* Journal of Environmental Management, 18, 581–594.

Zhang, F., Yan, X., Zeng, C., Zhang, M., Shrestha, S., Devkota, L.P. & Yao, T., 2012. *Influence of traffic activity on heavy metal concentration of roadside farmland soil in mountainous areas*. International Journal of Environmental Research And Public Health, 9, 1715–1731.

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