

PRZEMYSŁAW WINIAREK\*, ANETA KRUK

PKP Polskie Linie Kolejowe S.A., ul. Targowa 74, 03-734 Warszawa

## Pesticide residues in soils along railway lines

*Abstract:* The aim of the study was to examine the content of pesticide residue in soil adherent to the railway track down to the depth of 2 m below ground. The two lines selected for the examination differed in properties determining pesticide content. To assess the scale of influence of the chemical treatment applied, the selected lines were outside intensive farming areas. The examination consisted of testing the content of 2,4-D, MCPA, carbofuran and atrazine using liquid chromatography, and the content of phenol, cresols, DDT/DDE/DDD, aldrin, dieldrin, endrin and HCH using gas chromatography. The content of 2,4-D, MCPA and phenol was below  $0.01 \text{ mg}\cdot\text{kg}^{-1}$ , cresols – below  $0.03 \text{ mg}\cdot\text{kg}^{-1}$ , DDT/DDE/DDD – below  $0.024 \text{ mg}\cdot\text{kg}^{-1}$ , aldrin and dieldrin – below  $0.004 \text{ mg}\cdot\text{kg}^{-1}$ , endrin – below  $0.005 \text{ mg}\cdot\text{kg}^{-1}$ , carbofuran and atrazine – below  $0.02 \text{ mg}\cdot\text{kg}^{-1}$ ,  $\Sigma\text{HCH}$  – below  $0.017 \text{ mg}\cdot\text{kg}^{-1}$ . The content of pesticide residue in soils along the examined railway lines is lower than that found in arable soils in Poland. No differences in the content of pesticide residue were found between the soils underneath the modernised railway line and the one which had been in use without major alterations to the upper layers for many years. The study found no evidence of any influence of chemical plant removal from railway lines on adjacent lands.

*Keywords:* railway line, pesticides, residue, soil

### INTRODUCTION

The railway network is a system of interconnected railway lines, stations, terminals, and different types of facilities necessary for ensuring its continuous operation. The primary aim of its existence is providing the possibility of safe transportation of persons and items. Railway lines are also places favouring the expansion of certain plant species as a result of spreading diaspores from nearby ecosystems (including arable fields) or as a result of their incidental transport from distant ecosystems (Fornal-Pieniak and Wysocki 2010). The development of the vegetation cover on transport routes depends on specific, difficult habitat conditions, particularly those of soil and moisture, contributing to limiting the abundance and type of the occurring plant species. In such areas, particularly grassy assemblages develop with a substantial contribution of ruderal vegetation and expansive invasive species. The expansion for forest species is also observed (Kryszak et al. 2006, Świąt and Majkutek 2006). Sowing of slopes of cuttings and embankments (Fig. 1) positively contributes to limiting the abundance of ruderal species and stability of railway facilities, and therefore traffic safety (Koda et al. 2010). However, the sown plants can negatively affect traffic safety by expanding onto the railway tracks uncontrollably. They can cause blockage of mechanical devices, or disturb the functioning of electrical and electronic devices for controlling railway traffic.

Moreover, the presence of vegetation on the interface of the running surface of the wheel (tread) and top of rail negatively affects the braking distance of trains. In the period of high temperatures, dry plants – particularly on railway lines with wooden sleepers – increase the risk of fires.

The problem with overgrowing railway tracks is observed both on lines exploited for many years and ones recently subject to investment processes. In addition to the elimination of conditions favouring plant vegetation during reconstruction of railway lines, infrastructure managers of the infrastructure also apply mechanical removal of undesired vegetation through its mowing. Mechanical methods do not guarantee efficient elimination of weeds on long sections of railway lines over a short period of time. The problem is particularly important on railway lines with heavy traffic. For reduction of risk to employees and for efficiency, it is popular and effective to chemically remove vegetation by means of devices moving on the railway line. Advantages of this type of devices include direct dosage of plant protection chemicals in a very narrow belt of railway tracks, and the possibility of dynamic unplugging of the dosing devices in places requiring particular protection.

In spite of long-lasting application of chemical vegetation removal on railway lines, no properly planned research has been performed so far concerning soils and pesticide content in railway areas. Lack of

\* *Mgr inż. P. Winiarek, przemyslaw.winiarek@plk-sa.pl*

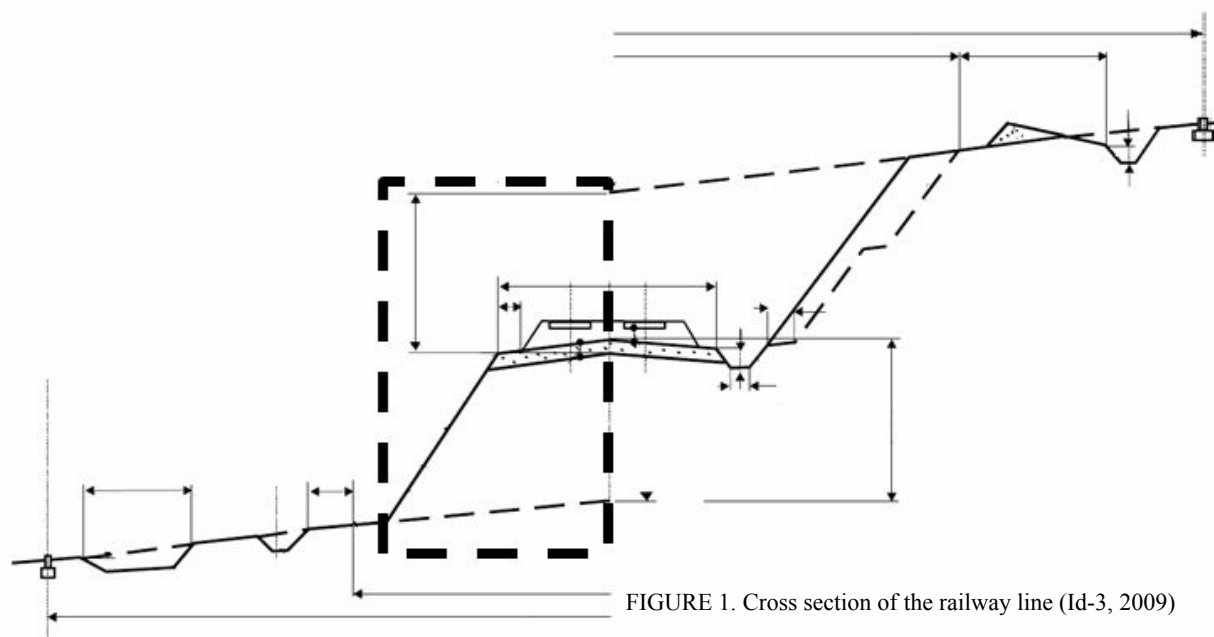


FIGURE 1. Cross section of the railway line (Id-3, 2009)

results of soil research and assessment of an increase in pesticide content over time from the construction or reconstruction of a railway line is evident. Research on railway lines to date has been particularly limited to urban and industrial areas, and railway junctions with intensive human impact. This makes it difficult to conduct discussion and compare study results (Zhang et. al. 2012) and to assess the potential effect of arable land, subject to the most intensive application of pesticides. Current studies on contaminants related to railway lines cover particularly polycyclic aromatic hydrocarbons (PAHs) and heavy metals (Malawska and Wiłkomirski 1997, 2000, 2001; Brooks 2004 Bukowiecki et al. 2007, Moret et al. 2007, Akoto et. al. 2008, Liu et al. 2009, Wiłkomirski 2010). Data on contamination with pesticides are limited. Published study results concerning soils on railway lines, in spite of their exclusion from agricultural production, particularly concern the uppermost layer of the soil profile down to a depth of 0.5 m below ground level, analogically to research on arable soils. Such an approach makes it impossible to assess the degree of contamination of deeper parts of the profile, and transport of contaminants to shallow groundwaters. In the case of a railway line, the upper part of the embankment is not a native formation. They are formations with predefined construction parameters, relevantly compacted and usually elevated above the adherent areas.

The study objective was to fill the information gap and assess pesticide residue in the soil and the underlying formations down to a depth of 2 m below ground level, directly at the railway track. The study covered two railway lines: one subject to reconstruction affecting the soil profile in the period 2000–2008,

and one exploited for many years without changes in the soil profile. The assessment of the scale of effect of chemical treatments performed on railway tracks covered railway lines running outside areas of intensive agricultural production.

## STUDY AREA

The study area covered railway lines included in the trans-European railway system operating international traffic. Samples for analyses were collected in October 2014 on railway line No. 6 Zielonka-Kuźnica Białostocka along the section between the Bug River and railway station Małkinia, and along railway line No. 2 Warszawa Centralna-Terespol on the section from the Mienia River to railway station Mrozy. A single and double track fragment of the railway line was selected, as well as fragments with wooden and concrete sleepers. Both of the railway lines are characterised by a mixed traffic structure combining passenger and freight transport. Railway line No. 6 was constructed in 1862, and line No. 2 in the period 1866–1867. Plant protection chemicals for removal of redundant vegetation had been applied for many years on both lines (PKP Polskie Linie Kolejowe S.A. 2009). Railway line No. 2 in the designated location was subject to reconstruction in the years 2000–2008. Railway line No. 6 is being prepared for construction works on the rail tracks. Both of the lines in the designated locations run across rivers. The designated sections run through forest and arable areas with very low intensity of agricultural activity, outside agglomerations and pollution sources.

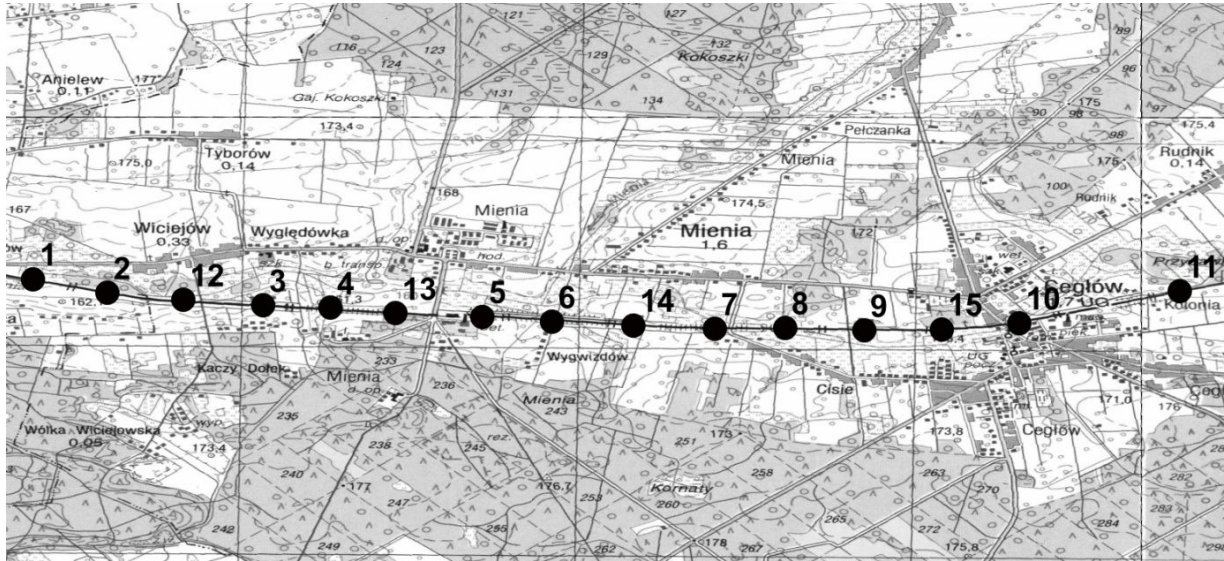


FIGURE 2. Location of sampling sites on railway line No. 2

In each of the designated locations, 15 soil samples were collected alternatively on both sides of railway tracks directly at the track and in front of the drainage system (Fig. 2 and 3). On railway line No. 2, soil samples were collected at distance intervals of 450 m between the line of traction poles and the drainage system. One sampling site was located outside the drainage system: control sample No. 13 representing areas other than railway areas, where no pesticides were used. In the case of railway line No. 6, samples were collected every 200 m on average – one (No. 1) sample was collected under the railway bridge directly

at the Bug River channel, and another one in the area between railway tracks – intertrack space (No. 12).

#### MATERIALS AND METHODS

Sample collection and laboratory analyses were performed by an accredited laboratory as defined in the Act of 30 August 2002 (Ustawa..., 2002). Planning of sample collection was conducted in accordance with guidelines included in norm PN-ISO 10381-1:2008. Samples from a depth of 0–2 m below ground level were collected in accordance with

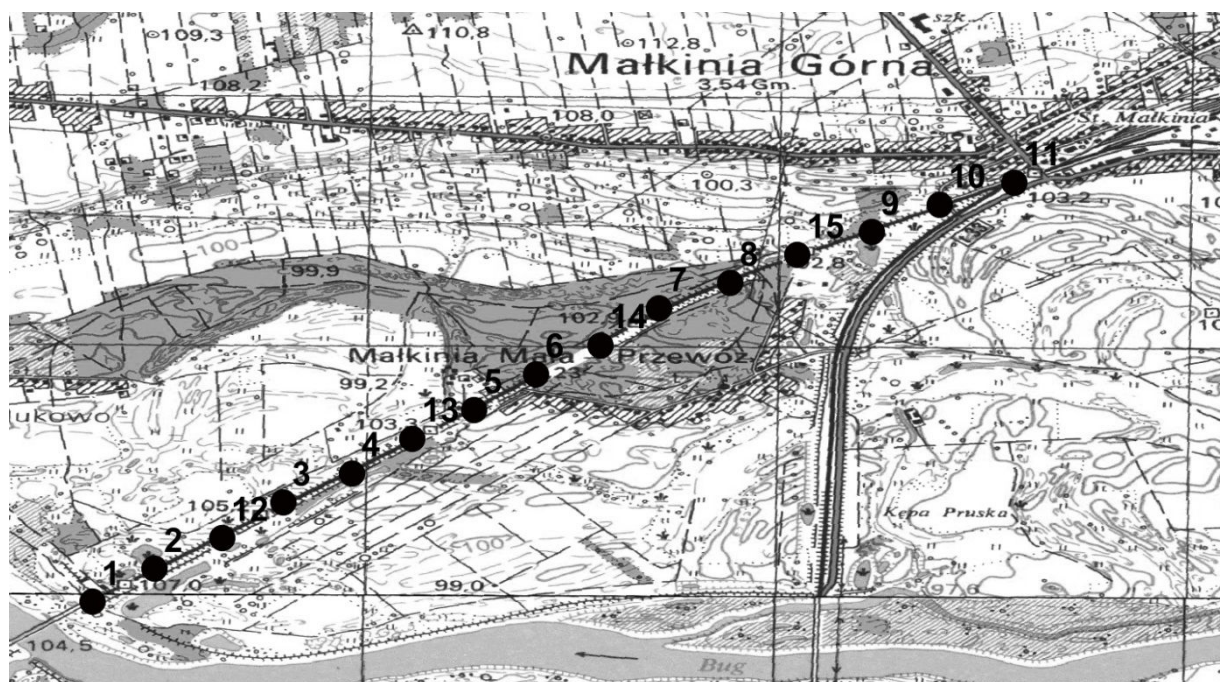


FIGURE 3. Location of sampling sites on railway line No. 6

guidelines included in norm PN-ISO 10381-5:2009. The representative sample was prepared by mixing and reduction of the collective sample from a depth of 0–2 m below ground level. At each location, one representative sample was taken by means of a manual soil core sampler. The analyses focused on pesticides for which legally accepted contents in soils were determined. For each section of the railway line, in 15 samples, the content of the following substances was determined (Table 1):

- 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) by means of highly efficient liquid chromatography with mass spectrometry;
- phenol and cresols (sum of ortho, meta, para) by means of gas chromatography with mass spectrometry.

For each section of the railway line, in four samples, the content of the following was additionally determined:

- DDT/DDE/DDD, aldrin, dieldrin, endrin, alpha/beta/gamma HCH by means of gas chromatography with mass spectrometry;
- carbofuran and atrazine by means of highly efficient liquid chromatography.

## RESULTS AND DISCUSSION

Soil collected along railway lines No. 2 and 6 meets quality standards for transport areas specified

in the Regulation of the Minister of the Environment of 9 September 2002 binding on the date of the research, and Regulation of the Minister of the Environment of 1 September 2016 binding on the date of preparation of the article (Table 2–4). In spite of many years of application of plant protection chemicals, the obtained results show that soils related to railway lines meet not only norms for transport areas, but also with a large measure of safety the most rigorous norms specified for areas categorised as arable land.

2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA) commonly used in herbicides (Sitarek 2004) were reported in amounts lower than  $0.01 \text{ mg}\cdot\text{kg}^{-1}$ . In research conducted in arable fields (soil developed from light and medium loam), Kucharski and Urbanowicz (2008) found the presence of MCPA at a level of up to  $0.014 \text{ mg}\cdot\text{kg}^{-1}$ .

Similarly low contents were observed in the case of phenol and cresols. They varied from  $<0.01$  to  $0.077 \text{ mg}\cdot\text{kg}^{-1}$  for phenol, and  $<0.03 \text{ mg}\cdot\text{kg}^{-1}$  for cresols. The amounts were respectively 5000 and 1700 times lower than the accepted values specified in the Regulation of the Minister of the Environment of 9 September 2002 for transport areas (group C). Very low content was recorded for atrazine – below  $0.02 \text{ mg}\cdot\text{kg}^{-1}$ .

The content of the remaining compounds in soil, namely aldrin, dieldrin, HCH: alpha, beta, gamma was lower than  $0.004 \text{ mg}\cdot\text{kg}^{-1}$ , endrin lower than  $0.005$

TABLE 1. Characteristics of analytical methods for the determination of pesticide residues (SGS, 2014)

Parameter	Laboratory equipment	Limit of detection – LOD ( $\text{mg}\cdot\text{kg}^{-1}$ )	Limit of quantification – LOQ ( $\text{mg}\cdot\text{kg}^{-1}$ )	Analyte recovery (%)	Precision (%)	Accuracy (%)
2,4-D	LC-MS/MS	0.001	0.01	112.8	3.19	98.5
MCPA				98.4	5.09	100
Phenol	GC-MS Agilent 7890/5973 MSD	0.003	0.01	103	6.8	94.1
Cresols				108	5.4	94
DDT		0.001	0.004	109	5.1	96.1
DDE				82–107	2.4–2.6	95–96.1
DDD				87.7	3	102
Aldrin				115	3.7	95.4
Dieldrin				113	4.2	101.1
Endrin				96.7	7.6	97.2
alpha-HCH				109	4.4	96.5
beta-HCH				109	4.8	98.5
gamma-HCH				90.2	5.6	98.9
Carbofuran				HPCL Shimadzu SIL20+MS/MS AB Sciex QTRAP4000	0.002	0.02
Atrazine	97.3	3.24	–			



mg·kg<sup>-1</sup>, DDT/DDE/DDD (sum of isomers) lower than 0.024 mg·kg<sup>-1</sup>, and carbofuran lower than 0.02 mg·kg<sup>-1</sup>.

The comparison of study results concerning soils collected from railway areas with study results referring to 214 samples of arable soils of Poland presented by Maliszewska-Kordybach et al. (2013a, 2013b) shows that the contents of selected pesticide residues are lower in soils from railway areas than the maximum contents reported in arable soils. For example, in arable soils, the maximum content of  $\alpha$ -HCH amounted to 0.151 mg·kg<sup>-1</sup>, total HCH – 0.15208 mg·kg<sup>-1</sup>, sum of DDT, DDE, DDD – 0.45009 mg·kg<sup>-1</sup>, whereas the content in the studied soils under railway lines amounted to <0.004 mg·kg<sup>-1</sup>, <0.017 mg·kg<sup>-1</sup>, and <0.024 mg·kg<sup>-1</sup>, respectively. A similar dependency is observed in the case of forest soils and in urban areas. In the soil of forest complexes, Witczak et al. (2005) observed the content of the compounds at a level of up to 0.00823 mg·kg<sup>-1</sup>, 0.00823 mg·kg<sup>-1</sup>, and 0.1202 mg·kg<sup>-1</sup>, respectively. Kawano et al. (2000) determined total HCH in arable soils at a level of up to 0.027 mg·kg<sup>-1</sup>, in forest soils up to 0.006 mg·kg<sup>-1</sup>, in urban soils up to 0.015 mg·kg<sup>-1</sup>, and total DDT, DDE, and DDD respectively 1.7 mg·kg<sup>-1</sup>, 0.66 mg·kg<sup>-1</sup>, and 0.67 mg·kg<sup>-1</sup>.

No differences were determined in the content of the analysed compounds between railway lines No. 2 and 6 (rebuilt line and line exploited for many years with no considerable interference in the surface formations). Replacement of railway ballast coming in direct contact with pesticides, renewal of the subballast, and works in deeper layers of the profile show no considerable effect on the content of residue of plant protection chemicals. The parameters of soil in the direct vicinity of rail tracks subject to many years of treatment with the application of plant protection chemicals are comparable with results for soil near rebuilt railway line where new construction materials were used, having no contact with pesticides before. Therefore, the obtained results do not confirm the occurrence of the phenomenon of contaminant accumulation in soil as a result of many years of application of pesticides.

Constant content of pesticide residue along the analysed sections of railway lines was determined (no spatial variability). This suggests no occurrence of locally intensified eluviation of the studied compounds from the soil. This is caused by the high compaction of soils under the railway line resulting from construction norms for railway structures, and their heating to high temperatures, limiting the process of infiltration of the mixture of water and pesticide into the soil.

No content of the analysed compounds in samples collected on the railway line higher than for those collected in their vicinity was recorded. The fact is confirmed by study results for sample No. 13 collected at railway line No. 2 (located on the side of a forest), representing soils not directly related to railway and agriculture, not subject to the application of pesticides. The sample was collected outside the drainage system of the railway line, constituting the boundary of runoff of precipitation and melt waters as well as shallow groundwaters from the railway line. All of the determined compounds in sample No. 13 as well as in the remaining 14 samples collected on the line occurred on the same level. Lack of an increase in the content of pesticide residue in the direct vicinity of the line results from that fact that in treatments on railway lines, plant protection chemicals were applied very precisely on the narrow belt of land along the railway line. The movement of spraying devices on even railway tracks limits the horizontal movement of the units dispensing the agent, and therefore the effect of wind on its uncontrolled migration outside the rail tracks. Research on quality of waters by the Massachusetts Department of Agricultural Resources (2006) in the place of their crossing by railway lines subject to the application of selected herbicides (more than 300 samples over a period of eight months) showed that the buffer zone of approximately 3 m around the stream where chemical treatment is discontinued can be sufficient to provide its proper protection against pesticides from railway tracks. It is also important that railway lines are usually perpendicular to streams, and not parallel as it is usually the case on arable land. This eliminates the possibility of fast supply of contaminants with surface flow and waters of fast circulation in the catchment.

## CONCLUSIONS

1. The content of pesticide residue in the soils of the analysed railway area is lower than the acceptable value for transport areas determined by legal regulation.
2. The content of pesticide residue in the soils of the analysed railway area is lower than in the arable soils of Poland analysed by IUNG-PIB.
3. No differences were determined in the content of pesticide residue in soils under the rebuilt line and that subject to many years of exploitation with no substantial interference in the surface formations. No phenomenon of contaminant accumulation in the soil was determined.
4. No change in the content of pesticide residue was observed along the analysed railway lines (no spatial

variability). This suggests no occurrence of locally intensified eluviation of the analysed compounds from the soil.

5. No effect of treatments of chemical vegetation removal from railway lines on the adherent areas was determined. The content of pesticide residue in soils in the railway area and soils directly outside the railway ditch serving as the drainage system of the railway line and local barrier for the migration of contaminants was determined on a uniform low level.
6. It is recommended to conduct research on pesticide content in the water flowing out from the railway line as a function of time passed since the chemical vegetation removal.

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## Pozostałości pestycydów w glebach wzdłuż linii kolejowych

*Streszczenie:* Celem badań była ocena zawartości pozostałości pestycydów w glebie i utworach podścielających do głębokości 2 m p.p.t. bezpośrednio przy torze kolejowym. Do badań wytypowano dwie linie kolejowe przebiegające poza obszarami intensywnej produkcji rolnej. Oznaczono zawartość 2,4-D, MCPA, karbofuranu, atrazyny z wykorzystaniem chromatografii cieczowej, fenolu, krezoli, DDT/DDE/DDD, aldryny, dieldryny, endryny, HCH z wykorzystaniem chromatografii gazowej. Zawartość 2,4-D, MCPA, fenolu była poniżej  $0,01 \text{ mg}\cdot\text{kg}^{-1}$ , krezoli poniżej  $0,03 \text{ mg}\cdot\text{kg}^{-1}$ , DDT/DDE/DDD poniżej  $0,024 \text{ mg}\cdot\text{kg}^{-1}$ , aldryny i dieldryny poniżej  $0,004 \text{ mg}\cdot\text{kg}^{-1}$ , endryny poniżej  $0,005 \text{ mg}\cdot\text{kg}^{-1}$ , karbofuranu i atrazyny poniżej  $0,02 \text{ mg}\cdot\text{kg}^{-1}$ ,  $\Sigma \text{HCH}$  poniżej  $0,017 \text{ mg}\cdot\text{kg}^{-1}$ . Poziom pozostałości pestycydów w glebach wzdłuż badanych linii kolejowych był niższy niż w glebach ornym Polski. Nie stwierdzono różnic w zawartości pozostałości pestycydów w glebach pod linią zmodernizowaną i eksploatowaną od wielu lat bez znaczącej ingerencji w utwory powierzchniowe. Nie stwierdzono oddziaływania zabiegów chemicznego usuwania roślinności z linii kolejowych na tereny sąsiednie.

*Słowa kluczowe:* linia kolejowa, pestycydy, pozostałości, gleba