Investigated was the soil at an old metallurgical landfill site of CMC Sisak Ltd. which has been exposed to the direct influence of metallurgical nonhazardous waste for many years. Concentrations of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) after extraction in aqua regia were determined. Heavy metal concentrations, except Hg, were determined by inductively coupled optical emission spectrometry and inductively coupled plasma mass spectrometry (ICP-OES, ICP-MS). Concentration of Hg was determined by atomic absorption spectrometry.

Our objective was to assess the pollution level according to the potentially unacceptable risk limit levels for industrially used soil prescribed by the Croatian Soil Monitoring Program, and levels permitted by some EU member countries.

The results of heavy metal concentrations in composite samples of landfill soil were also compared with the results obtained from the reference sample taken in the nearby park, outside the battery limits. The obtained results qualify the analysed landfill soil as contaminated with Cu according to the legislation of all observed EU countries, with Cd according to the legislation of Italy, Poland, and Belgium (Wallonia), and with Cr according to the legislation of Finland and Poland. To allow future use of the landfill certain measures of soil treatment will be necessary.

Key words: Soil, pollution, landfill, nonhazardous waste
sites in areas called industrial landfills/dumps. Although this waste contains high levels of heavy metals (Hg, Pb, Cr, Ni, Zn, Cd, Cu), most of the former or existing metallurgical landfills/dumps, areas which may extend over several hectares, are now abandoned without adequate safety measures and their environmental impact has been poorly studied.

Consequently, as the potential hazardousness of these highly polluted sites is still largely unknown, it is very difficult to propose remediation techniques or new occupational plans. Unfortunately, according to the available papers in Europe, only a few dump sites of metallurgical factories have been extensively examined, both for their heavy metals content and speciation, and for their pedological characteristics.12,13,18–20

According to E. Remon et al.,14 the only way to influence or minimize the presence, i.e. concentration of toxic heavy metal is to control and stabilize the existing landfill areas. In this respect, restoration of an adequate plant cover21,22 could be an effective alternative in treating polluted metallurgical landfills, which could serve dual objectives. The first is a sustainable site reclamation, and the second a visual improvement of highly degraded areas.

We investigated the soil at an old metallurgical landfill area (size of active area about 3000 m²) of CMC Sisak Ltd., which has been exposed to the direct influence of metallurgical non-hazardous waste for a long time. Our objective was to determine the content of the heavy metals by chemical extraction procedures as a first step towards assessing the pollution, as well as choosing methods for its treatment and preparation for continued industrial use in accordance with applicable Croatian laws.

**Experimental**

**Sampling**

The soil was sampled after waste removal and cleaning of the landfill where the nonhazardous waste from the steel and pipe production processes had been disposed. This unordered, so-called factory landfill had served as a disposal site for several types of industrial nonhazardous waste over a period of 50 years (waste key number: 10 02 02 – unprocessed slag; 10 02 10 – mill scales; 16 11 04 – other linings and refractory from metallurgical processes; 19 09 02 sludges from water clarification; 19 09 03 – sludges from decarbonation). In addition to industrial waste, the examined site was also used for disposing other nonhazardous waste, mainly generated from maintenance, reconstruction, and building of new production lines and buildings (15 01 03 – wooden packaging; 20 01 01 – paper and cardboard; 20 01 39 – plastics; 20 03 07 – bulky waste; 17 01 07 – mixture of concrete, bricks, tiles and ceramics). In addition to industrial waste, the examined site was also used for disposing other nonhazardous waste, mainly generated from maintenance, reconstruction, and building of new production lines and buildings (15 01 03 – wooden packaging; 20 01 01 – paper and cardboard; 20 01 39 – plastics; 20 03 07 – bulky waste; 17 01 07 – mixture of concrete, bricks, tiles and ceramics). In addition to industrial waste, the examined site was also used for disposing other nonhazardous waste, mainly generated from maintenance, reconstruction, and building of new production lines and buildings (15 01 03 – wooden packaging; 20 01 01 – paper and cardboard; 20 01 39 – plastics; 20 03 07 – bulky waste; 17 01 07 – mixture of concrete, bricks, tiles and ceramics).

After waste removal and landfill cleaning (Fig. 2), sampling of individual soil samples, and the forming of average soil samples was organized according to the directions given by the Croatian Soil Monitoring Program.23

Considering the size of the investigated polluted area (about 3000 m²) and recommendations given by the Croatian Soil Monitoring Program23 on the average number of
area around the melt shop and pipe mill. Sampling density for B1–B9 was 4 samples/km² with 5 sub-samples (one composite sample of 1500 g) at the sampling site, collected from each corner and the centre of the square (2 m × 2 m). Concentrations of heavy metals were determined (Cd, Cr, Cu, Hg, Ni, Pb and Zn) both in those samples and in the composite samples from the landfill.

In addition, one reference sample was collected from the surface layer (callow) 0–10 cm at the sampling site collected from each corner and the centre of the square 2 m × 2 m in a nearby park outside the CMC Sisak Ltd. battery limits approximately 1500 m air-line distance in north-west direction. Activities carried out at the landfill have no direct influence on the park where the reference sample was collected, and as such represent the soil image of a wider area. The reference soil sample was collected in the same manner as samples used for preparation of composite samples.

**Cd, Cr, Cu, Hg, Ni, Pb, and Zn concentrations**

Concentrations of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) for samples A1, A2, and the reference sample, after extraction in *aqua regia* according to the HRN ISO 11466:2004 standard (Soil quality – Extraction of trace elements soluble in *aqua regia*) were determined. Heavy metal concentrations, except Hg, were determined by inductively coupled optical emission spectrometry according to the HRN EN ISO 11885:2010 standard (Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry) using a Perkin-Elmer Optima 7000 DV ICP-OES apparatus. The concentration of Hg was determined by atomic absorption spectrometry, HRN EN 1483:2008 standard (Water quality – Method using atomic absorption spectrometry) on a Perkin-Elmer Atomic absorption spectrophotometer with Varian hydride-vapour generation system.

The B1–B9 composite samples were air-dried (<40 °C), sieved (<2 mm), homogenized and after *aqua regia* digestion for low and ultra-low determinations on soils, sediments and lean rocks were analysed by ICP-MS (Acme laboratories, Vancouver, Canada).

**Results and discussion**

To determine the pollution level of any ecosystem component, including soil, it is necessary to determine the influence of pollution on human health. This is done in order to determine the limit values of a particular pollutant at which, based on scientific knowledge, there is not even the slightest possible risk of harmful effect on human health and/or the environment.

Croatian legislation defines the Ordinance on the Protection of Agricultural Land against Pollution as the only regulation defining the quality of agricultural soil. Limit values...
of pollutants, including heavy-metal concentration limits for soil used for industrial purposes are not prescribed.

In Croatia, there is no legal regulation directly related to monitoring soil condition and collection of data regarding potentially polluted or polluted soil. Problems with potentially polluted or polluted soil are only indirectly mentioned in legislation. Some EU member countries regulate the limit values of soil pollutants according to the land usage principle (agricultural, residential, recreational, etc.), which was adopted in the preparation of the Croatian Soil Monitoring Program.23

The aim of the measurements conducted during the research was to determine whether the disposed non-hazardous waste (unprocessed slag, mill scales, linings and refractories from metallurgical processes, sludge from water clarification, sludge from decarbonation, etc.) in the unprotected area represented a potential local source of anthropogenic pollution of the soil (despite its use for industrial purposes) and groundwaters. The Croatian Soil Monitoring Program was used for identification and interpretation of the results. Based on the potential sources of soil pollution and the type of possible pollutant emissions listed in the Program, the concentrations of Cd, Cr, Cu, Hg, Ni, Pb, and Zn as pollutants originating from metal industry were determined.

The results of landfill soil analysis were compared to the recommended limit values (LV) of soil pollutants allocated for industrial and commercial usage according to the Croatian Soil Monitoring Program (Table 1). Results for the determination of heavy metals in composite soil samples (A1 and A2) from the landfill area (Table 2) show that concentrations were mostly below limit values (LV) of soil pollutants in industrial and commercial areas according to the Croatian Soil Monitoring Program. Exceptions were concentrations of Cu and Cr, resp.

The determined heavy metal concentrations in the composite soil samples collected from the landfill area correspond to the results of most soil samples taken around the production facilities. Higher deviations were noticed for Cu and Cr, where concentrations in the landfill samples were higher than con-

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**Table 1** — Limit values (LV) of soil pollutants according to land usage

<table>
<thead>
<tr>
<th>Type of soil pollution</th>
<th>Agricultural land</th>
<th>Playground</th>
<th>Resident areas</th>
<th>Parks and recreation areas</th>
<th>Industrial and commercial areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vrste onečišćenja u tlu</td>
<td>Tlo za poljoprivrednu proizvodnju</td>
<td>Igralište</td>
<td>Područje stanovanja</td>
<td>Parkovi i rekreacijska područja</td>
<td>Područja industrijske i komercijalne primjene</td>
</tr>
<tr>
<td>Metali izlučeni u zlatotopci</td>
<td>Metal content in soil (dry matter) / mg kg⁻¹</td>
<td>Udjel u suhoj tvari / mg kg⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd and compounds</td>
<td>&lt;5</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Cd i spojevi</td>
<td>&lt;5</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Hg and compounds</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Hg i spojevi</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Pb and compounds</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Pb i spojevi</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Ni and compounds</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Ni i spojevi</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Cu and compounds</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Cu i spojevi</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Total Cr</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Ukupni Cr</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Zn and compounds</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Zn i spojevi</td>
<td>&lt;5</td>
<td>10</td>
<td>50</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>
centrations found in the samples taken from around the production facilities. Measured Cu concentrations at the landfill area were 916 mg kg\(^{-1}\) of dry matter in sample A1, and 1018 mg kg\(^{-1}\) of dry matter in A2, while concentrations in the samples from around the production facilities ranged from 19.06 mg kg\(^{-1}\) (B8) to 916 mg kg\(^{-1}\) of dry matter (B5).

The similar was found for Cr. Measured Cr concentrations for A1 amounted to 756 mg kg\(^{-1}\) and A2 766 mg kg\(^{-1}\), while for samples from production facilities 35.70 mg kg\(^{-1}\) (B8) to 262 mg kg\(^{-1}\) of dry matter (B7).

For Zn the opposite situation was noticed. Measured Zn concentrations for A1 amounted 78.01 mg kg\(^{-1}\) and A2 296 mg kg\(^{-1}\), while the Zn concentrations in samples from around the production facilities ranged from 115 mg kg\(^{-1}\) (B2) to 10 000 mg kg\(^{-1}\) of dry matter in sample B7 taken from the area near the plant for galvanization of welded pipes. Such a high concentration of Zn is the result of the direct pollution with Zn from the stack of the furnace system for hot galvanization of welded pipes.

The obtained results for heavy metal concentrations are presented in Table 3, and compared to the limit values for potentially unacceptable risk for soil used in industry according to the Croatian Soil Monitoring Program.\(^{23}\)

The comparison of heavy metal concentrations in composite soil samples from the landfill area with values (LV) representing a potentially unacceptable risk for soil allocated for industrial and commercial usage (Table 4) shows that the measured concentrations of Hg, Pb and Zn were lower than LV regulated by Belgium, Finland, Italy, Poland and United Kingdom, i.e. all considered countries which have regulated LV for heavy metals.

For Zn the opposite situation was noticed. Measured Zn concentrations for A1 amounted 78.01 mg kg\(^{-1}\) and A2 296 mg kg\(^{-1}\), while the Zn concentrations in samples from around the production facilities ranged from 115 mg kg\(^{-1}\) (B2) to 10 000 mg kg\(^{-1}\) of dry matter in sample B7 taken from the area near the plant for galvanization of welded pipes. Such a high concentration of Zn is the result of the direct pollution with Zn from the stack of the furnace system for hot galvanization of welded pipes.

The obtained results for heavy metal concentrations are presented in Table 3, and compared to the limit values for potentially unacceptable risk for soil used in industry according to the Croatian Soil Monitoring Program.\(^{23}\) It could be concluded that the landfill is polluted with Cu and Cr, while the area around the production facilities is polluted with Zn.

Before comparing the heavy-metal concentrations in the composite soil samples from the landfill area with those outside battery limits, it is necessary to compare the results obtained for the reference samples with the LV in soil allocated for industrial and commercial usage (Table 4).

Values of heavy metals in reference samples shown in Table 4 are significantly lower than the LV of tested metals for industrially and commercially used soil according to the Croatian Soil Monitoring Program.\(^{23}\)

For pollution assessment, a comparison of the heavy metal content in composite soil samples from the landfill with the values for potentially unacceptable risk for soils allocated for industry regulated by some EU member countries\(^{25}\) is given in Table 5.

The comparison of heavy metal concentrations in composite soil samples from the landfill area with values (LV) representing a potentially unacceptable risk for soil allocated for industrial use regulated by some EU member countries shows that the measured concentrations of Hg, Pb and Zn were lower than LV regulated by Belgium, Finland, Italy, Poland and United Kingdom, i.e. all considered countries which have regulated LV for heavy metals.

Concentrations of Cd in the landfill soil samples marked as A1 and A2 were below the LV representing a potentially unacceptable risk for soil allocated for industrial use regulated by Belgium, Finland and United Kingdom, but higher than LV regulated by Italy and Poland. Therefore, from the point of view of Poland and Italy, the landfill area is considered polluted.
The results obtained for Ni concentrations in the landfill soil classify this soil as polluted according to LV regulated by Finland and Poland, while compared to other observed EU countries, these concentrations were lower than regulated LV.

The landfill area is considered polluted with Cu because the measured concentrations exceeded the LV representing a potentially unacceptable risk for soil allocated for industry regulated by all observed EU countries.

Concentrations of Cr in the landfill soil samples were below LV for potentially unacceptable risk for soil allocated for industry regulated by Belgium (Brussels), Italy and United Kingdom, but higher than LV regulated by Belgium (Wallonia), Finland and Poland.

**Conclusion**

Soil pollution in the Republic of Croatia is defined only for agricultural land by the Ordinance on the Protection of Agricultural Land against Pollution, while the quality of soil for industrial purposes is not regulated.

To evaluate the soil pollution level of the landfill area used for temporary storage of nonhazardous waste (10 02 02 – unprocessed slag; 10 02 10 – mill scales; 15 01 03 – wooden packaging; 16 11 04 – other linings and refractories from metallurgical processes; 17 01 07 – mixture of concrete, bricks, tiles and ceramics; 19 09 02 – sludge from water clarification; 19 09 03 – sludge from decarbonation; 20 01 01 – paper and cardboard, 20 01 39 – plastics; 20 03 07 – bulky waste) over many years of metallurgical production, a comparison was made of heavy metal concentrations from landfill soil samples with LV for potentially unacceptable risk for soil allocated for industry according to the Croatian Soil Monitoring Program and regulated LV in some EU countries. In addition, the results were compared with heavy metal concentrations in soil taken from around production facilities and a reference sample collected outside battery limits. According to the obtained results, the following conclusions may be drawn:

- The determined heavy metal content in composite soil samples A1 and A2 of landfill soil show that concentrations were mostly below the LV of pollutants for industrially and commercially used soils according to the Croatian Soil Monitoring Program. Exceptions were Cu and Cr concentrations which were higher than LV;
- The determined heavy metal concentrations in composite soil samples from the landfill area mainly correspond those determined in soil samples collected around the production facilities;
- Higher deviation in Cu and Cr concentrations were noticed in landfill soil samples, where the values exceeded concentrations in soil from around the production facilities;
- Zn concentrations in landfill soil are lower than the highest measured concentrations in the soil samples taken from an area nearby galvanization;
- Comparison heavy metal concentrations in composite soil samples from the landfill with values for potentially unacceptable risk for soil allocated for industrial use, regulated by some EU member countries, show that measured Hg, Pb and Zn concentrations were lower than LV regulated by Belgium, Finland, Italy, Poland and United Kingdom i.e. all considered countries which have regulated LV for heavy metals;

<table>
<thead>
<tr>
<th>Elements</th>
<th>Landfill Odlagalište</th>
<th>Samples Uzorci</th>
<th>Reference sample Referentni uzorak</th>
<th>Belgium/Brussels Belgija/Brisel</th>
<th>Belgium/Wallonia Belgija/Walonija</th>
<th>Finland Finska</th>
<th>Italy Italija</th>
<th>Poland Polska</th>
<th>United Kingdom Ujedinjeno Kraljevstvo</th>
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<tbody>
<tr>
<td>Cd</td>
<td>A1</td>
<td>19.33</td>
<td>&lt;0.001</td>
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<td>50</td>
<td>20</td>
<td>15</td>
<td>13</td>
<td>1400</td>
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<tr>
<td></td>
<td>A2</td>
<td>17.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Hg</td>
<td>A1</td>
<td>0.034</td>
<td>0.162</td>
<td>30</td>
<td>84</td>
<td>5</td>
<td>5</td>
<td>27</td>
<td>480</td>
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<tr>
<td></td>
<td>A2</td>
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<td></td>
</tr>
<tr>
<td>Pb</td>
<td>A1</td>
<td>24.73</td>
<td>49.82</td>
<td>2500</td>
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<td>81.62</td>
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<td>Ni</td>
<td>A1</td>
<td>313</td>
<td>34.14</td>
<td>700</td>
<td>500</td>
<td>150</td>
<td>500</td>
<td>285</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>399</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cu</td>
<td>A1</td>
<td>916</td>
<td>21.09</td>
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<td>500</td>
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<td>1018</td>
<td></td>
<td></td>
<td></td>
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<td>Cr</td>
<td>A1</td>
<td>756</td>
<td>57.84</td>
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<td>700</td>
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<td>800</td>
<td>475</td>
<td>5000</td>
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<td>A2</td>
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<td></td>
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<tr>
<td>Zn</td>
<td>A1</td>
<td>78.01</td>
<td>284</td>
<td>3000</td>
<td>1300</td>
<td>400</td>
<td>1500</td>
<td>1650</td>
<td>–</td>
</tr>
</tbody>
</table>

The results obtained for Ni concentrations in the landfill soil classify this soil as polluted according to LV regulated by Finland and Poland, while compared to other observed EU countries, these concentrations were lower than regulated LV.
– Cd concentrations in landfill soil samples were below LV for potentially unacceptable risk for soil allocated for industrial use regulated by Belgium, Finland and United Kingdom, but higher than LV regulated by Italy and Poland; therefore, from the point of view of Poland and Italy, the landfill area is considered polluted;
– The determined Ni concentrations in the landfill soil classify this soil as polluted according to LV regulated by Finland and Poland, while in comparison to other observed EU countries, these concentrations were lower than the regulated LV;
– The landfill area is considered polluted with Cu because the measured concentrations exceed LV for potentially unacceptable risk for soil allocated for industry regulated by all observed EU countries;
– Cr concentrations in the landfill soil samples were below LV for potentially unacceptable risk for soil used in industry according to Croatian Soil Monitoring Program, has led to the conclusion that the landfill is polluted with Cu and Cr;
– Regarding the obtained results for the landfill and owner’s decision on future usage of the examined area, certain measures in further treatment of soil have to be taken if required by law.

References

Literatura

SAŽETAK

Onečišćenje tla kao posljedica odlaganja neopasnog otpada iz procesa proizvodnje čelika

T. Sofilić,a I. Brnardić,b* V. Šimunić-Mežnarićc i A. Šoršad

Ispitano je tlo starog metalurškog odlagališta tvornice CMC Sisak d. o. o., koje je dugi niz godina bilo izloženo različitim utjecajima neštetnog metalurškog otpada. Sadržaj teških metala Cd, Cr, Cu, Hg, Ni, Pb i Zn u tlu određen je u uzorcima tla nakon njihove ekstrakcije metala zlatotopkom. Određivanje sadržaja svih navedenih metala osim žive provedeno je metodom optičke emisijske spektrometrije induktivno vezane plazme (ICP-OES), dok je sadržaj žive određen spektrometrijom atomskog apsorpcija (AAS) primjenom hidridne tehnike.

Da bi se procijenila razina onečišćenja tla, napravljena je usporedba rezultata sadržaja teških metala u analiziranim uzorcima tla s propisanim vrijednostima za potencijalno neprihvatljiv rizik za tlo upotrebavano u industriji prema Programu trajnog motrenja tla Republike Hrvatske kao i prema propisanim vrijednostima u nekim zemljama EU. Rezultati određivanja sadržaja teških metala u kompozitnim uzorcima tla uspoređivani su s njihovim koncentracijama u referentnom uzorku tla uzetom s prostora obližnjeg parka, izvan tvorničkog kruga. Dobiveni rezultati svrstavaju analizirano tlo s odlagališta kontaminiranim prema propisima svih promatranih zemalja EU-a s bakrom, Italije i Poljske s kadmijem i Belgije (Valonija), Finske i Poljske s kromom. Za buduću upotrebu tla u istu svrhu moraju se poduzeti odgovarajuće mjere.

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