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Land Reclamation

Achieving Sustainable Benefits

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Reclamation of Pb/Zn smelter wastes in Upper Silesia, Poland

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ABSTRACT: Water and wind erosion of toxic smelter waste is an urgent environmental problem in the Silesia region of Poland. Two differing (Welz and Doerschel process) Pb/Zn smelter wastes were stabilized in 1994 by application of heavy loads of $CaCO_3$ (30 Mg ha^{-1}), CaO (1.5 - 15 Mg ha^{-1}), and municipal sewage sludge (150 - 300 Mg ha^{-1}), followed by seeding with acid- and salt-tolerant grasses. Laboratory experiments demonstrated that amendments with CaO can effectively reduce metal solubility to ppb levels, however, the use of $CaCO_3$ alone did not sufficiently suppress metal solubility. The revegetation of much of the Doerschel material area failed initially, so the area was capped with waste lime and retreated with sludge (300 Mg ha^{-1}) in 1995. Standing biomass averaged 3.3 Mg ha^{-1} and 2.9 Mg ha^{-1} in the fall of 1997 for the Welz and Doerschel wastes, respectively.

1 INTRODUCTION

The Upper Silesia region (Gorny Slask) is located in southwestern Poland (Figure 1). Although it occupies only about 2% of Poland's territory, it is home to over 10% of the country's population and is the nation's main industrial center. It has rich deposits of coal, zinc and lead. Today it is a vast agglomeration of mines, steel works, smelters, chemical plants and other industries. The City of Katowice (population 380,000) is the political center of the District which covers 14 cities and a number of neighboring towns which merge into a large metropolitan area with a population over three million. Waste disposal in industrialized areas of eastern and central European countries has been a serious environmental issue for decades. The Katowice District in Upper Silesia is an example of environmental consequences caused by uncontrolled industrial activity with little or no effort to protect the environment (Ochrona 1993). It has been estimated that over 90% of the solid waste material produced by the entire heavy industry and mining sector in Poland has been deposited in Upper Silesia. A small percentage of these sites, particularly coal processing waste dumps, have been reclaimed by the use of thin topsoil lifts (30 cm) to cover the fill surface. However, this traditional method is expensive, and not always successful (Patrzalek & Strzyszcz 1980; Strzyszcz 1980). The majority of mining waste sites are potentially phytotoxic and very difficult to revegetate by traditional means. As a result, large areas of mining wastes remain exposed to wind erosion and to the leaching of toxic constituents by rain waters. Therefore, losses of metalliferous dust to the surrounding community coupled with minimization of direct contact by children playing on the piles has become a major priority for the local environmental protection units.

Due to the change in socio-political structure and the associated emphasis on cleaning up surface waters, 30 new wastewater treatment plants will be constructed in Upper Silesia by the year 2000 and will increase the sludge quantity from current levels (40,000 Mg yr^{-1}) to > 100,000 Mg yr^{-1} . While this provides an obvious solid waste disposal challenge, it also could simultaneously provide an opportunity for reclaiming the mining waste piles, if appropriate protocols can be developed.

This research/demonstration program has been implemented as a sub-project of Project Silesia, a cooperative effort between the USEPA, USAID, the Polish national government and the Department of Ecology in Katowice, Upper Silesia, Poland (Pantuck et al. 1996). The reclamation of various mining wastes with municipal sewage sludge biosolids along with appropriate liming treatments has been proven effective in a variety of locations in the USA (Daniels et al. 1989; Sopper 1992). The data and results presented in this paper summarize our efforts to come up with a viable and cost effective technology for the revegetation of mining and smelter wastes with these two materials. Application of lime and sewage sludge to reclaim waste piles seemed to be an excellent alternative for topsoiling; however, our preliminary observations showed that implementing this method on smelter sites would require extensive research on waste geochemistry as well as selection of metal-tolerant plant cultivars.

2 EXPERIMENTAL METHODS

Over the spring and summer of 1994 two experiments were established at a Pb/Zn smelter site in the Katowice area to evaluate the potential for utilizing local sewage sludge and liming materials for revegetation. Two contiguous sites with a total area of 2 ha were selected at the Orzel Bialy Smelter waste pile. The area selected was covered by two different zinc and lead smelter waste materials from (1) Doerschel furnace and (2) Welz process smelting technologies between 1950 and 1985. The area was completely barren of vegetation. Before the installation of experiments, over 160 point samples (from 0 - 5 and 20 - 25 cm) were collected on a 10 m grid and analyzed for pH, and total S, Zn, Cd, and Pb. Water-soluble forms of Cd, Zn, Pb, Na and SO_4^{2-} were also measured by extracting the material with water using a 1:2 (w/v) ratio. Electric conductivity was also measured in these water extracts. All methods followed those of Page et al. (1982). In addition, we analyzed composite samples from each waste type for potential acidity by a modified hydrogen peroxide oxidation technique (Smith et al. 1974).

The Welz material was pH 6.9 with a total-S content of 2.26% which presumably was almost entirely sulfate since the potential acidity generated by H_2O_2 oxidation was negligible. The Doerschel waste, on the other hand, was pH 3.6 with a total-S content of 10.7 %. The potential acidity of the Doerschel material was equivalent to 25 Mg of calcium carbonate equivalent per 1000 Mg of waste material when oxidized and titrated to pH 6.0, but the liming demand increased to 75 Mg per 1000 Mg when titrated to pH 7.0. This seemingly incongruous behavior was attributed to the dis-aggregation of the smelter waste structure to some extent at increasing pH, releasing

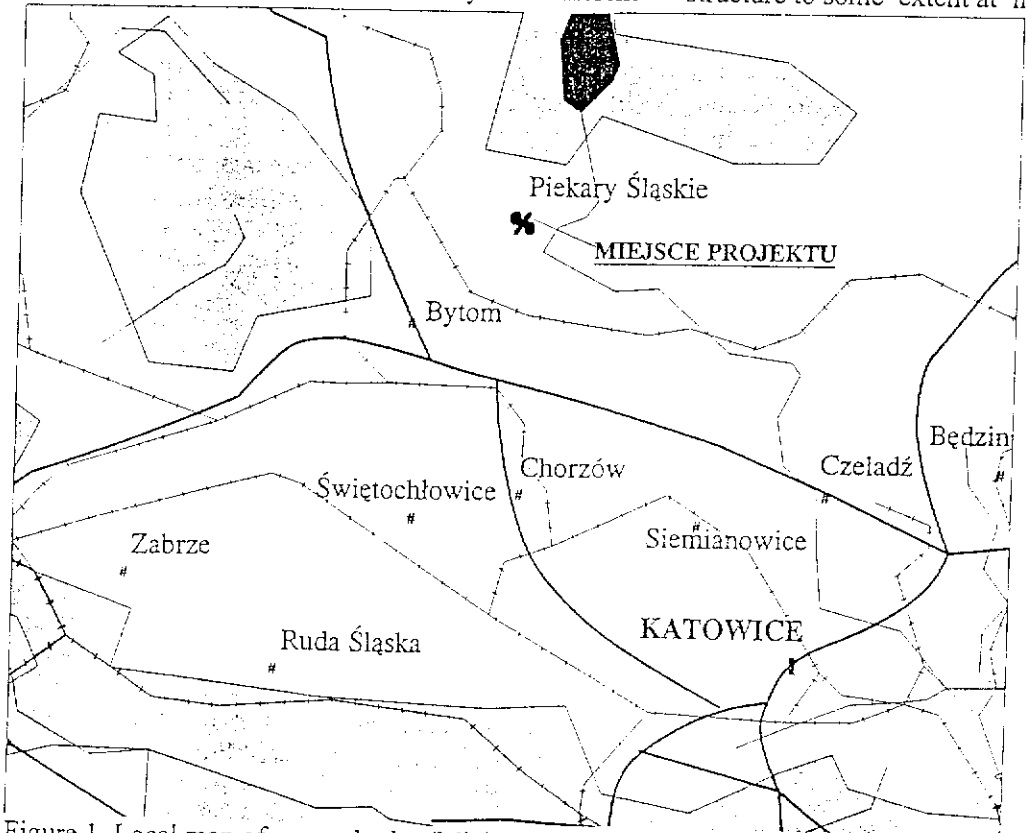

Figure 1. Local map of research plot (Miejsce Projektu) location in Katowice area in southern Poland.

reduced S to solution from previously occluded forms. Based on our assessment of these waste chemical properties and the local site conditions, the following reclamation treatments were implemented on 0.5 ha of each waste:

1. pH adjustment by application of 30 Mg ha^{-1} $CaCO_3$ and 15 Mg ha^{-1} CaO for the waste from the Doerschel furnace; and 30 Mg ha^{-1} of $CaCO_3$ and 1.5 Mg ha^{-1} of CaO for waste produced by the Welz process. This was then followed by application of sewage sludge at 0, 150, or 300 Mg ha^{-1} to 1/3 of each demonstration area.

2. Lime and sludge amendments were incorporated with a chisel plow. Higher sludge rates were applied in split applications to ensure appropriate incorporation.

3. Seeding with metal- and salt-tolerant grasses was conducted in the fall of 1994. Grass cultivars were selected from short-term (90 day) germination/growth tests using waste material as a growing medium as discussed later in this paper (Table 1).

In addition to the large demonstration plots on the smelter wastes described above, a replicated small plot experiment (30 m x 120 m) in a randomized complete block design was installed on both Welz and Doerschel wastes to evaluate sludge loading rates, lime addition rates and grass species effects and interactions. The extreme spatial variability of chemical properties of the wastes, however, did not allow conclusions to be drawn based on classical statistical analysis. Therefore, spatial analysis was used to interpret the data as shown in Figure 2. Before plot treatment, and at the end of each growing season, a monitoring program was conducted at each of the 10 m grid locations to measure above-ground biomass, metal content in plants, and changes of waste chemical properties including pH, metal solubility, and salinity. Data reported in Tables 2-5 are generated from these grid samples.

In order to find an effective method for reducing metal mobility and toxicity in these smelter wastes, several laboratory experiments were conducted using different amounts of CaO or $CaCO_3$ as waste amendments. Increasing amounts of CaO or $CaCO_3$ were added to 100 g samples of smelter waste materials which had been previously mixed with 60 g of sludge on a dry basis. Mixtures were equilibrated in a water slurry (1:2 ratio) by heating to 60° C and stirring on a magnetic stirrer. Resulting solutions were centrifuged and analyzed for pH, EC, and soluble Cd, Zn and Pb (Page et al. 1982).

A greenhouse pot experiment with Welz material was performed to characterize the growth response of a number of grass and legume cultivars grown in a high metal and high salinity environment. Germination and biomass production were observed over a 90 day period. One subset of pots was spiked with 2% $NaSO_4$ to simulate conditions typical of Doerschel materials. Electrical conductivity (EC) as high as 16 dS m^{-1} (mmho cm^{-1}) has been observed in samples from this site. A total of the 20 different species were tested, with those shown in Table 1 selected for further use in the field trials.

3 RESULTS AND DISCUSSION

A number of 20 grass cultivars that were tested in the pot experiment seem to be useful for revegetation purposes and exhibited different degrees of adaptation to chemical stress (Table 1). A mixture of the most acid/salt tolerant species was used in the field trials discussed later. Additional detailed studies are ongoing on plant material adaptation at the field site.

The survey of the raw waste deposits showed that Doerschel and Welz material can contain extremely large amounts of Zn, Cd, and Pb (Table 2). Doerschel material is much higher in these metals than Welz. This material also had high EC resulting from high amounts of soluble salts that can dramatically inhibit plant growth (Bolt 1991). The demonstration plots and randomized complete block experiment were installed on both Welz and Doerschel wastes at this site. However, vegetation did not survive on the Doerschel material (Figure 2), most likely due to the initial high salinity (16 dS m^{-1}) and metal toxicity related primarily to water soluble Zn (1670 mg kg^{-1}) and Cd (108 mg kg^{-1}, Table 3).

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It is important to note that the reason for adding lime to the Welz waste was to completely suppress water soluble metals, even though the initial pH was near neutral. Also, due to the fact that the ground-water quality below and around the waste piles

Table 1. Resistance of different grass species to salinity and heavy metals

Grass species (cultivars)	Tolerance to metals	Tolerance to salinity
Lolium perenne (Solen)	+++*	+++
Lolium perenne (Argona)	+++	+++
Lolium multiflorum (Telga)	++	++
Lolium multiflorum (Koga)	++	++
Lolium x boucheanum Kunth. (Mega)	++	++
Poa pratensis (Alicja)	+++	-
Festuca rubra (Atra)	+	-
Festuca arundinacea (SZD 492)	++	+
Festuca ovina (Sima)	++	-

*degree of tolerance - Relative tolerance of seedlings to elevated Pb and Zn in soil solution and EC > 4.0 dS m^{-1}. Species with +++ exhibited little, if any, phytotoxicity symptoms while species with + were clearly suppressed.

Table 2. Total metal content in waste materials sampled before treatment

Waste material	Zinc (g kg^{-1})		Cadmium (g kg^{-1})		Lead (g kg^{-1})	
	average	range	average	range	average	range
Welz	30.9	6.9-128	0.54	0.058-2.76	7.9	2.6-16.5
Doerschel	75.1	13.0-126	2.31	0.66-3.46	23.82	7.09-40.6

Table 3. Chemical properties of waste material sampled before (1994) and after (1995) amendment with sewage sludge and lime

Waste material	Sampling time	Soluble zinc mg kg^{-1}	Soluble cadmium mg kg^{-1}	Soluble lead mg kg^{-1}	pH	EC
Welz	Before	343	17.6	1.8	7.0	7.3
	After	279	17.7	1.1	7.2	3.5
Doerschel	Before	1670	108	5.4	5.8	16
	After	983	57.4	2.9	6.0	9.0

*values reported reflect averages of about 80 samples of each material

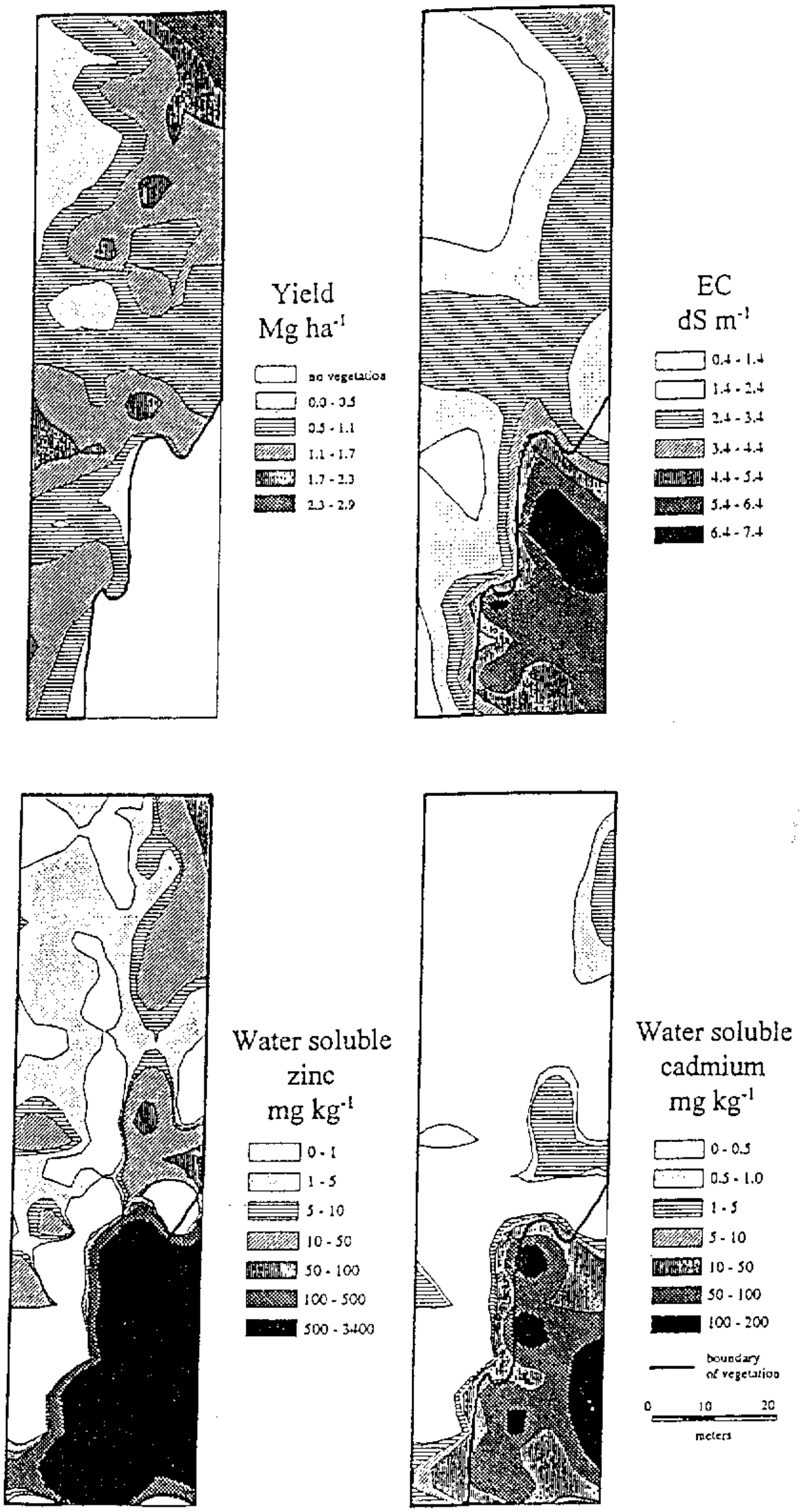

Figure 2. Standing biomass and soil chemical properties over the experimental area sampled in the late summer of 1995, one year after treatment and revegetation. Spatial plot is based on 160 point samples taken on a 10 m grid. The lower right hand corner of the block was dominated by Doerschel waste with associated high salinity and metal levels. The black line indicates the vegetated boundary. Note the strong association of metal levels with the vegetated boundary position. The reason for the low productivity in the upper left hand corner of the plots on Welz waste is not clear. However, this region was very low in soil sized (<2 mm) materials and sludge incorporation was poor in this zone compared to the rest of the plot area.

has been seriously degraded by decades of deep mining and uncontrolled waste disposal, no effort was made in this study to document the "ground-water effects" of our treatments. Local and regional ground-water quality is an important issue to local authorities (Ochrona 1993), and future studies in the program will assess the net water quality impacts of these stabilization approaches. However, the direct short term human health risk from blowing metalliferous dust coupled with sediment loss to surface waters has been deemed so severe that surface revegetation and stabilization of the piles is of overwhelming importance to local environmental authorities.

Adverse physical properties of the Doerschel material, particularly high compaction and cementation also contributed to total inhibition of plant growth. Lime plus sludge at the rates used was not effective for establishment of vegetation. However, the combined treatment reduced solubility of some metals which may decrease the potential of metal leaching from these piles. It should be emphasized that changes in pH and Cd solubility in both Doerschel and Welz materials were smaller than expected. Calcium carbonate seemed not to be effective in control of pH and metal mobility in such materials, most likely due to limited solubility and occlusion with iron oxides that are present in these waste materials. Laboratory experiments demonstrated that heavy rates of $CaCO_3$ did not result in substantial increase of pH and reduction of Zn and Cd solubility, whereas CaO reduced metal mobility to ppb levels (Figure 3). However, this effect may be temporary since the CaO buffering system will change with time in the field into $CaCO_3$ via hydrolysis and CO_2 sorption. This seems very likely since the addition of CaO along with $CaCO_3$ to the field plots did not affect initial pH and metal mobility to any great extent after the first year (Table 3).

Vegetation was successfully established on 85% of the Welz material area (Figure 2), even though it was high in water soluble Zn, Cd, and other salts as indicated by high EC (Figure 2). Average standing biomass was 0.8, 2.9, and 3.4 Mg ha^{-1} in the fall of 1995, 1996, and 1997, respectively (Table 4). Heavy metal levels in plant tissue were elevated (Table 4) as would be expected, but appeared stable over time. Visual symptoms consistent with Zn phytotoxicity were apparent in the first and second years, particularly on the boundary between well- and poorly-vegetated areas. The spatial variability present in the waste piles under study provided a unique opportunity to characterize the extent of plant

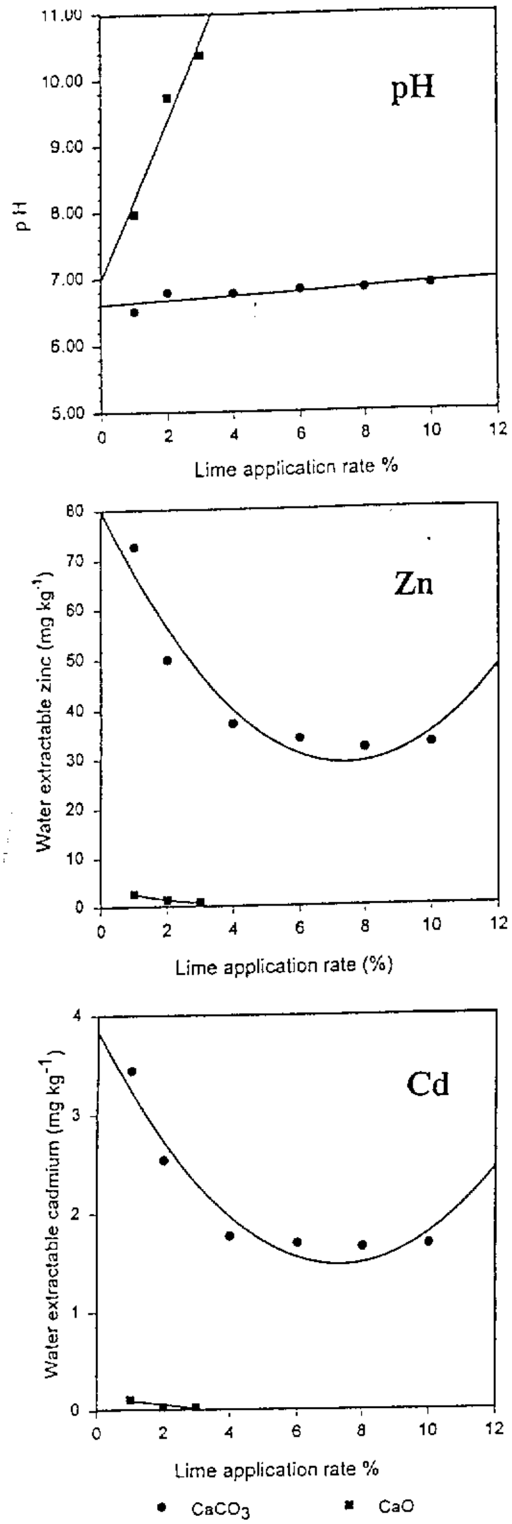

Figure 3. Influence of lime rate and type on pH and water soluble metal levels in Welz waste. These relationships point out the importance of driving the pH to levels > 7.0 to limit Zn and Cd solubility, even though the original pH was 6.6. The data also point out the relative inability of $CaCO_3$ alone to affect pH in this metalliferous system.

resistance to this harsh environment. It seems obvious from our spatial analysis that soluble Zn, Cd, and high salinity are the most limiting factors controlling the effectiveness of revegetation of zinc smelter wastes (Figure 2). However, it is also obvious that these elements co-vary together and cannot be isolated as being singularly phytotoxic. From this analysis it is reasonable to conclude that the grass cultivars used can adapt to the relatively harmful conditions as characterized by chemical properties of the Welz material (Table 5).

The Doerschel waste area was retreated in 1995 with a 15 cm cap of waste lime ($CaO + CaCO_3$) which subsequently received 300 Mg ha^{-1} municipal sludge. The sludge was incorporated into the lime cap and seeded to the same tolerant seed mix (Table 1) used in 1994. This treatment resulted in 75 to 80% ground cover by the spring of 1996 with little evidence of metal toxicity in the vegetation. Standing biomass in the fall of 1996 averaged 4.5 Mg ha^{-1}, but declined slightly (3.0 Mg ha^{-1}) in 1997. On-site soil evaluation indicated that the roots penetrated to the lime/waste interface, but no more than 2 cm into the underlying Doerschel material. Thus, the ability of the treatment to sustain the vegetative community through summer droughts will need to be evaluated over time. The Welz waste area was similarly evaluated in 1996 and continued to support vigorous herbaceous vegetation, including legumes. It was also noted that a number of perennial herbaceous and woody species invaded the plots from the surrounding area, supporting the hypothesis that the chemistry of these materials has been sufficiently stabilized to support long term plant growth. Plant roots penetrated into the treated Welz materials to a depth of 10 to 20 cm.

4 CONCLUSIONS

Based upon the results of these studies, a recommendation for one-time application of lime and stabilized sewage sludge that has undergone appropriate pathogen reduction and meets regulatory heavy metal loading limits for the rate applied is made. The rates of lime and sludge should be calculated based on a detailed survey of particular waste chemical properties. For extremely toxic waste such as Doerschel material, heavy rates of lime with a significant CaO component, are recommended to ensure the revegetation and reduction of toxicity. Several more years will be required to evaluate the full results of the restoration trials in the Katowice area and to optimize the draft sludge utilization guidelines that have been developed (Pantuck et al. 1996). However, it is clear that locally produced sewage sludge biosolids can be effectively used in combination with heavy liming at many mining and industrial waste piles in this region to drastically reduce wind and water erosion losses of toxic solid wastes to surrounding communities. This option is much less expensive than thick topsoiling or other material reprocessing alternatives currently available. Finally, this approach can simultaneously solve the current and impending sludge management problems faced by this region.

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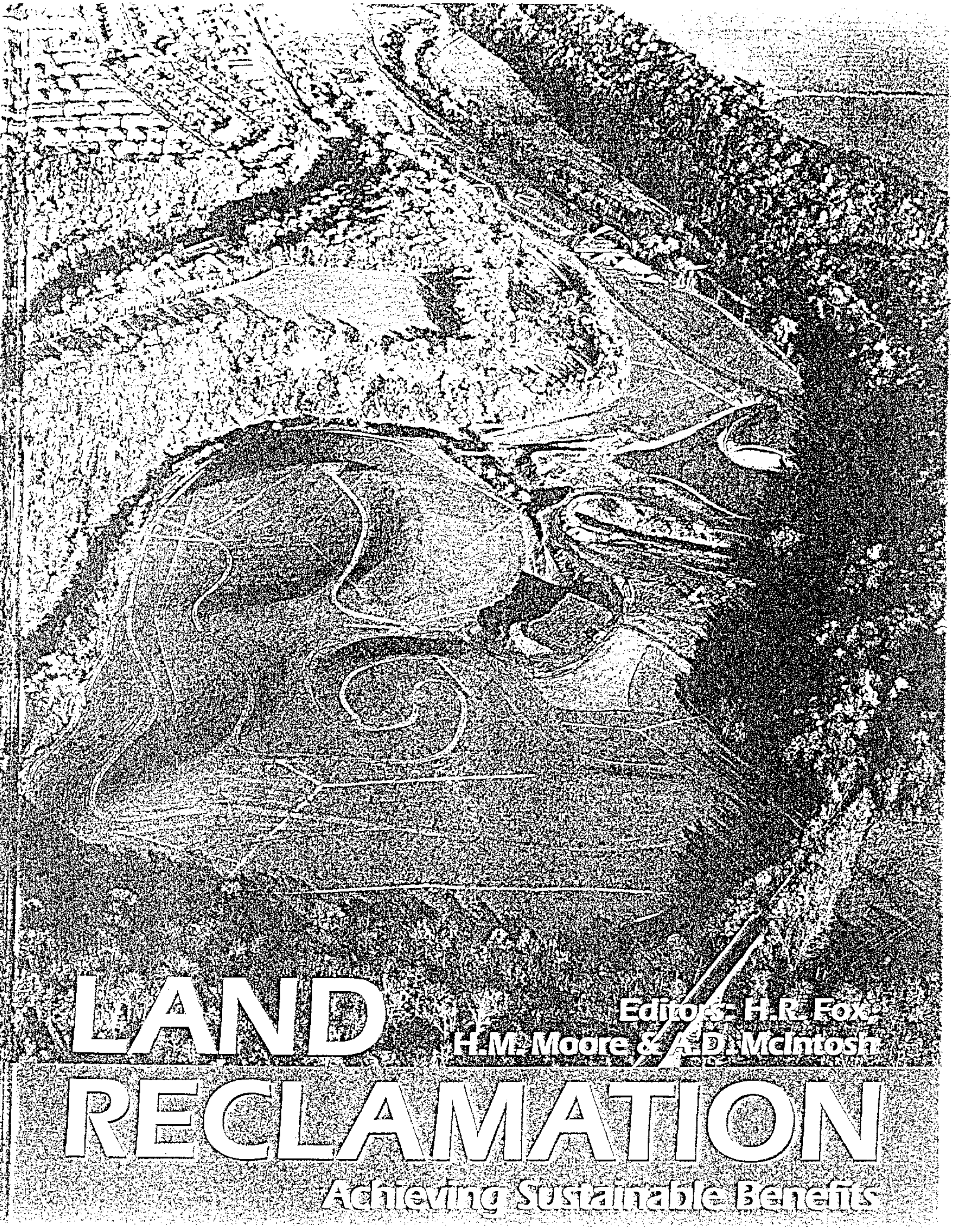
Table 4. Total mean biomass yield and levels of selected heavy metals in plant tissue

Welz Waste	**1995**	**1996**	**1997**
Yield (Mg ha^{-1})	0.80	2.88	3.37
Cd (mg kg^{-1})	4.7	3.7	3.3
Pb (mg kg^{-1})	31	26	35
Zn (mg kg^{-1})	228	166	184
Doerschel Waste	**1995***	**1996**	**1997**
Yield (Mg ha^{-1})	-	4.47	2.97
Cd (mg kg^{-1})	-	4.3	4.6
Pb (mg kg^{-1})	-	118	62
Zn (mg kg^{-1})	-	276	237

*revegetation completely failed in 1994/1995 and this portion of the site was re-treated with biosolids and lime.

Table 5. Maximum levels of chemical properties within vegetated areas

Zinc mg kg^{-1}		Cadmium mg kg^{-1}		Lead mg kg^{-1}		Soluble sodium mg kg^{-1}	Soluble sulfates mg kg^{-1}	EC dS m^{-1}
total	sol..	total	sol.	total	sol.			
100.000	1.000	1700	55	11000	3.7	1600	20000	5.4



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