Phytoremediation experiments on a slightly contaminated test field of a former uranium mining site

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Abstract Large sites with a slight contamination of heavy metals and metall(oid)s were in the past a problem for remediation measures – the "traditional" processes are too expensive for an application on such spaceous areas. Phytoremediation can be an alternative solution for such sites with slight contamination problems. The investigated field site is a former U mining area in East Germany. On this area, a low grade uranium ore leaching dump was situated, which was later removed during the remediation process of the area. Now, a slightly to moderately contaminated underground with restrictions of land use is remaining. Plant experiments with *Triticale*, *Helianthus annuus* and *Brassica juncea* were performed revealing the influence of biological additives (fungi, bacteria) and soil amendment strategies (increasing pH and organic matter, fertilizing) on biomass production and plant tolerance to heavy metals. Finally, Triticale was well suited as a phytoremediation plant on this site, due to its good adaptation to the acidic test field conditions, the high production of plant biomass and increased amount of extracted heavy metals per area. In lysimeter experiments it was figured out, that the different soil improvement strategies resulted in a reduction of the concentration of contaminants in the seepage waters, as well as of the seepage water rates and loads. In fermentation experiments for the further utilization of heavy metal loaded *Triticale* from the test field site, 89 %and 91.5 % yield of bioethanol was achieved in comparison with *Triticale* from an uncontaminated field. Hence, a further utilization of the plants from phytoremediation measures for the winning of bioenergy is feasible.

Key Words Phytoremediation, soil additives, heavy metals, radionuclides, utilization of plant biomass from phytoremediation, bioenergy

Introduction

In the last 20 years, remediation techniques for the treatment of sites contaminated with heavy metals made considerable progress. But very large contaminated sites represent up today a problem due to the high costs for their remediation. The most utilized strategies for this purpose are the set-aside of agricultural land or a large-scale covering, as it was carried out at the former uranium mining area in the south of East Germany. Phytoremediation represents an emerging and sustainable technology for slightly contaminated sites, where a selective utilization of plants for the remediation is performed. The low costs are one advantage of phytoremediation compared to the "classical" remediation methods. The long treatment time and the limited depth of activity are some disadvantages of this method. Phytoremediation is improving the physical, chemical and ecological quality of the soil, and allows a good integration into the landscape. A treatment of large areas is feasible, where other remediation methods operate too expensive. Hence, phytoremediation has a high future potential; it is innovative, saves nature and environment and represents a sustainable technology (Maeger 2000, Miller 1996).

Phytoremediation is differently interacting with soil and heavy metals/radionuclides (HM/R):

1. Phytoextraction of metall(oid)s
2. Phytostabilization (sequestration processes by plant roots) and immobilization of the metall(oid)s
3. Improvement of evapotranspiration and thus decrease of the seepage water rate
4. Substantial improvement of the natural soil quality

Higher heavy metal concentrations, extreme pH values and high salt concentrations in combination with limited amounts of nutrients are representing limiting factors for the phytoremediation. Hence, an application of this method is recommended especially on slightly contaminated areas (Puschenreiter 2003).

The site of investigation – a former U mining site

Phytoremediation investigations are carried out on a test field at a former uranium mining site. During the uranium mining in Germany from 1946—1990, over 113.000t U were produced in the mining area of Ronneburg and Seelingstaedt in the south of East Germany (Jakubick 1997). Low grade ores containing radionuclides were leached during the time from 1971 – 1990 at the site investigated here; the heap was called "Gessenhalde". The leachates contained enhanced concentrations of HM/R, which penetrated the barrier soil and which were retained in the glacial sediments underneath. The precipitating Fe-minerals accumulated higher amounts of HM/R due to co-precipitation. After the closedown of mining 1991 the area was remediated, and the dump was removed, but the contaminated underground is still existing. Since a few years, the phytoremediation of this area is investigated (Carlsson 2005).

The groundwater of the test field site is partially acidified; a pH down to 3.37—5.23 was measured, the E_h reaches data up to 700 mV, and sulfate concentrations up to 14 g/L were detected. These environmental factors result in an enhanced stress for the plants in case of acidified and saline pore waters. The concentrations of the metals in the water phase are tolerable for plants; however, the enhanced Mn concentration in the soil (up to 3.05%) could result in some enhanced stress reactions. In general the site seems suitable for a phytoremediation; therefore experiments for such a remediation are carried out here.

Aim of this project is the investigation of the phytoremediation at such a site (with special interest in the behaviour of the uranium); this means the phytoextraction as well as the phytostabilization. The research work is carried out on a decontrolled area of the remediation program of the former uranium mining. Further objectives of the project are the investigation of the mass transport of heavy metals and radionuclides into the underground; lysimeter experiments are carried out for this purpose. Furthermore, the utilization of the metal loaded plant material shall be investigated, e.g. biogas and biofuel formation and the combustion, with a mass balance of the fate and behaviour of the HM/R. Plants to be tested are *Helianthus annuus*, *Triticale* (*Triticosecale*) and *Brassica juncea*.

Experimental setup

Within the scope of the project, a new area for phytoremediation experiments at the test site "Gessenwiese" in Thuringia/ Germany was established. All together ten plots with 2 m x 2 m x 1 m were installed. While one plot is treated with no plants, the other nine plots are handled with three different soil additives and were planted with identical plant mixtures (*Helianthus annuus*, *Triticale* and *Brassica juncea*), based on the results of pot experiments. The different used soil additives are (with three replications):

1. Test field soil (homogenized substrate), (TF)
2. Test field soil with mycorrhiza (*Glomus intraradices*) and a bacteria culture containing the strains *Streptomyces tendae F4* and *S. acidiscabies E13*, (TF + MS)
3. Test field soil with 10 kg/m² calcareous topsoil, (MIX)

In addition all plots were fertilized with 100 kg nitrogen-phosphor-potassium/ ha (NPK). All experiments are described in more detail in (Mirgorodsky 2010). For direct acquisition and determination of evapotranspiration (mm) and to quantify soil hydrological and hydrochemical parameters, a lysimeter station was installed which includes three weighable lysimeters with a surface of 0.5 m² and 100 cm in depth each. While one lysimeter contains an undisturbed soil monolith (extracted from the test site), two were filled with TF control in addition of calcareous topsoil (MIX) and MS (TF+MS), respectively.

Results of phytoremediation experiments

As expected, the HM/R mobility in soil changed with application of the different variations of soil amendments and biological additives (MIX, MS and NPK) in comparison to the homogenized substrate (TF control). The addition of calcareous topsoil as amendment to TF control decreased the heavy metal mobility significantly by increasing pH (pH 4.4 to pH 6.7), organic matter (3% to 10%) and cation exchange capacity CEC (21 mmol/kg to 64 mmol/kg). As a result, also the concentration of available metals, especially Al, Zn and Ni, has been reduced. Furthermore, the addition of fungi and microbes has a mobilization effect on Al (TF+MS+NPK), but a slightly immobilization effect on Ni and Zn. The fertilizing strategy (TF + NPK) has no further effects on bioavailability of potentially toxic elements in this case (Mirgorodsky 2010).

Triticale produced the highest plant biomass yield on the test field site with 4.2 t DW/ha/harvest for fertilizing (TF) and microbial strategies (TF+MS). It should be noticed that the whole test field was fertilized (NPK) and therefore the differences between the three soil amendments seem to be covered. *Triticale* achieved a higher biomass on the acidic soil than in MIX soil (3.4 t DW/ha/harvest). *Helianthus annuus* and *Brassica juncea* grew better on the MIX substrate (up to 0.7 t DW/ha/harvest) in opposite to *Triticale*. *Triticale* is known to prefer acidic soil, and does not need a warm soil to start germination in contrast to *Helianthus annuus* and *Brassica juncea*. Moreover, *Triticale* is a fast growing plant, and *Helianthus* and *Brassica juncea* seem to be more sensitive against competition than *Triticale*. For all these reasons, *Triticale* took the advantage in biomass productivity over the other two plants (Mirgorodsky 2010). With *Triticale*, a phytoextraction yield of Al of 1.05 kg/ha (TF) was achieved (Fig. 1), of 120 g/ha Zn (TF) (Fig. 1), and of 260 mg/ha U (Mix), respectively.

The lysimeter experiments resulted in a reduction of the concentration of contaminants in the seepage waters, as well as of the seepage water rates and loads due to the different soil amendments (Mirgorodsky 2010). The decrease of the contaminant concentrations in seepage waters is due to the different mobility of the HM/R at a changing pH value and an increasing binding to organic matter with the addition of topsoil; the soil additives also change the water holding capacity of the underground. As a result, the annual seepage water loads can be significantly reduced by one to two orders of magnitude.

Utilization of metal loaded biomass from phytoremediation experiments

A subsequent utilization of the plant biomass as CO_2-neutral energy source was investigated in following experiments. The utilization of the HM/R-loaded plant residues after the harvest can contribute to the minimization of wastes, to the winning of energy and material recycling, and therefore to a reduction of the remediation costs.

First utilization experiments were carried out with *Triticale* from the test field site "Gessenwiese" in bioethanol fermentation processes. In experiments with two *Triticale* fractions from the test field site (HM/R contents of the plants 165 and 318 mg/kg Al, 5 and 6 mg/kg Ni, 30 and 28 mg/kg Zn, 0.04 and 0.06 mg/kg U, respectively), and with a *Triticale* sample from a field with no HM/R contamination for comparison, the feasibility of the fermentation of a metal loaded phytoremediation biomass was tested, and the possible inhibition of the product yield should be investigated.

The highest product yield was achieved with the uncontaminated *Triticale* with 45.3 L/dt DW. The fermentation of *Triticale* samples from the test field site "Gessenwiese" resulted in 41.4 and 40.5 L/dt DW, which represent 91.5% and 89.5% of the yield of the uncontaminated material, re-

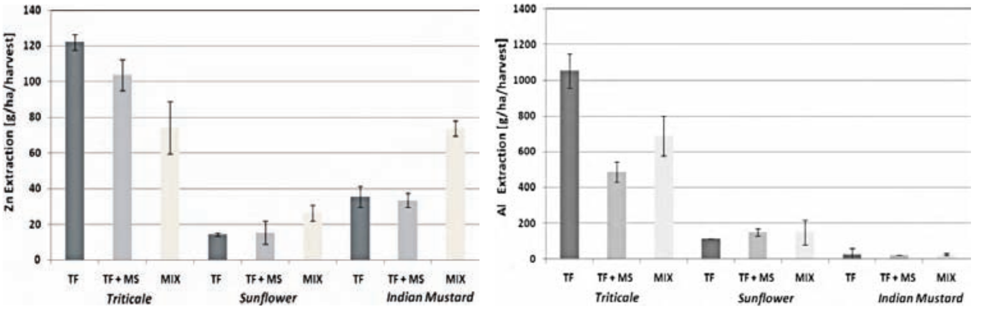

Figure 1 *Phytoextraction potential of selected plant species and different soil amendments for Al and Zn; all variances with NPK amendments*

spectively. The industrial standard yield for the fermentation of wheat, *Triticale* and rye is about 40 L/dt DW (Saatgut 2007); hence the obtained fermentation yields are still in the optimal range, and they would be economical in practice.

In further experiments, a possible inhibition of the fermentation process was investigated. For this purpose, the utilization of the carbohydrates in the fermentation suspension of *Triticale* loaded with heavy metals from the test field was measured. As a result, 96.8% of the usable sugars were consumed in the process, which is a nearly completely depletion of the utilizable carbohydrates. Hence, no inhibition could be observed in the fermentation process of *Triticale* with such heavy metal concentrations in the plant biomass. Thus, a utilization of the phytoremediation harvest from such a site for the winning of biofuels is feasible. In further experiments, the fate of the contaminants in the different off-products of such a process is investigated. Further experiments are also carried out in the field of biogas production from plant remainders of the phytoremediation harvest, as well as experiments for the combustion of the plant residuals.

Conclusions

At the test field site "Gessenwiese", which was investigated here, moderate heavy metal concentrations were measured, so that a phytoremediation is feasible. Field scale phytoremediation studies were carried out to investigate the suitability of different plant genotypes and soil additives for phytostabilization and/ or phytoextraction strategies. As a result, *Triticale* was well suited as a phytoremediation plant on this site, due to its good adaptation to the acidic test field conditions, the high production of plant biomass and increased amount of extracted HM/R per area. In lysimeter experiments it was figured out, that the different soil improvement strategies (microbiological strategies and soil amendments) resulted in a reduction of the concentration of contaminants in the seepage waters, as well as of the seepage water rates and loads.

In fermentation experiments for the further utilization of HM/R loaded *Triticale* from the test field site, 89 % and 91.5 % yield of bioethanol were achieved in comparison with *Triticale* from an uncontaminated field. These yields are in the optimal range for such a process, and they would be economical in practice. Hence, a further utilization of the plants from phytoremediation measures for the winning of bioenergy is feasible.

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