Dendroremediation of Metal and Metalloid Elements with Poplar and Willow in the Floodplain Area Downstream a Mining Hill, Tongling, China

L Kataweteetham\(^1\), G Rong\(^1\), J Zhu\(^1\), Y Chu\(^1,\*\) and Shengquan Liu\(^2\)

\(^1\)School of Resources and Environment, Anhui Agricultural University, Hefei, China
\(^2\)School of Forestry \& Landscape Architecture, Anhui Agricultural University, Hefei, China

\*Corresponding author

**Abstract.** Practical remediation technology is in great need to reclaim the land polluted with heavy metals and metalloids. Dendroremediation, the use of trees to remove pollutants from the environment is a cost-effective and eco-friendly technology. In this study, poplar and willow growing on the floodplain downstream a mining hill in Tongling city, China, as well as local soils were sampled to access the phytoextraction ability of different parts of the two tree species on \(\text{Cu, Zn, Cd and As}\). The results showed that both species of the trees grew well in spite of the stress from the high content of the toxic elements, especially \(\text{Cd and As}\). The root, bark, trunk, and branch of both species demonstrated Bio-concentration Factors (BCFs) of the four elements between 0.001 and 0.5, with \(\text{Cu and Zn}\) having higher BCFs than that of the other two elements and the bark and root having higher BCFs than the trunk and branch. Poplar showed relatively higher averaged BCFs than willow for all the elements, except \(\text{As}\), while willow had higher averaged Translocation Factors (TFs) than poplar. Though both species are not hyperaccumulators for these elements, they were considered suitable for soil remediation and forestation in this region.

1. **Introduction**

With rapid industrialization heavy metal/metalloid pollution has become a serious threat to the environment in many countries all over the world\(^{[1,2]}\). Excessive concentrations of the toxic elements, e.g. \(\text{Cd, Pb, Hg, Cr, Cu, Zn, and As}\), in soil and water can contribute to a variety of negative effects on living organisms in the food chain by bioaccumulation and biomagnification, and to the damage of ecosystems\(^{[2-4]}\).

Among the various sources of heavy metal/metalloid pollution, mining has been an important one, by which the previous precious arable land in the mining districts, as well as regions influenced by mining activities through flooding erosion and irrigation, has been made useless due to heavy pollution of toxic elements\(^{[4-5]}\). Tongling city, located in the middle and lower reaches of the Yangtze River, had been an important non-ferrous metal (copper) industrial base in China, which was rich in mineral resources and had more than 240 mines\(^{[6,7]}\). But with thirty years to more than half a century’s extensive exploiting, the mineral resources have been depleting and at the same time environmental pollution of heavy metals and metalloids, as well as ecological damage have become the prominent issues. Like many other mineral resources cities, Tongling has begun to transform its economic strategy selection and put environmental restoration and protection in an important position. In this
context, various effective and affordable technologies are urgently needed to recover the contaminated soil.

Phytoremediation, the use of green plants to remove pollutants from the environment or make them nontoxic, has increasingly been examined as a practical, cost-effective, and eco-friendly technology than the physical/chemical measures, such as soil replacement, solidification, and washing strategies\[^1-3\]. Dendroremediaiton, the use of trees in phytoremediation, is a potential practical technology, because of their specific characteristics such as fast rate of growth, the ability to grow on nutrient-poor soil, and deep root system\[^8,9\]. Reforestation in the mining area can also reduce erosion and contribute to the reduction of air pollution, as well as greenhouse gases\[^9\]. Many tree species, e.g. *Salix*, *Populus*, *Eucalyptus*, *Betula*, *Alnus*, and *Acer*, etc., have been found to have certain abilities to accumulate heavy metals and trace elements\[^9-12\]. Broad-leaved fast-growing tree species, such as *Populus* and *Salix*, and coniferous species, like *Pinus* demonstrated relatively good phytoextraction ability and are important species for further study and soil remediation application practices.

The main objectives of this study were to determine the phytoextraction ability of heavy metals/metalloids for poplar and willow growing in the floodplain district downstream a mining hill in Tongling city and to evaluate the possibility of using the two species for local soil restoration.

2. Material and Methods

2.1. Sampling Sites

Tree and soil samples were taken at Shifeng village, located in the floodplain area downstream a mine on Mudan hill, Tongling city. This was a metal mine, exploiting Cu, Au, Fe, etc. Mining and processing started in the early 1980s and stopped just two years ago. A river drains water as well as eroded materials from the mining area and flows through the flat floodplain area with various landuses, including rice fields, dry land, vegetable fields, etc. The distance from the mining area and the village is about 7 Km. The region is in the subtropical monsoon climate zone, with average annual air temperature being 16.4 °C and the average annual precipitation being 1368 mm\[^13\]. Floods usually happen in the spring and summer seasons, with intense rainfall and runoff being in summer, especially when monsoon is well developed. The fields and lands in the downstream area of the mine have been polluted from the mineral processing wastewater and even after the shutdown of the mine the river still flows pollutants from the disturbed surface, tailing heaps and dumps, especially by flood inundation. Besides, farmers have been irrigating the fields with the polluted river water.

Two sampling sites, namely A and B, are only about 400 meters apart. Both sites are near the river bank and fields.

2.2. Plant and Soil Sampling

Samples of two poplar trees (*Populus deltoids* cv. I-69/55) and one mixing soil sample were taken at site A and samples of two willow trees (*Salix babylonica* L.) and one mixing soil sample were taken at site B, in December 2018. The two poplar trees were about 20-30 meters in height and the two willow trees were about 5-10 meters in height. Root, trunk, bark and branch samples were taken from two poplar trees, namely poplar 1 and poplar 2 at site A, and from two willow trees, namely willow 1 and willow 2 at site B. Root samples were taken by digging into the root part with an earth-boring auger at two sides of the bottom of the trunk. Trunk growth cone samples at breast height (1.5 m) were collected by a Trephor. Bark samples were taken by a knife near the Trephoring site. The branches were collected by a handsaw at three different positions around the lower part of the tree crown. Soil samples were collected by earth boring auger with a depth of 0-60 cm at three separate locations in the sampling area to make a mixing sample for each site. All samples were carefully placed in labelled plastic bags before arriving at the laboratory for further treatment and analysis.

2.3. Pretreatment and Analysis

Root samples were first rinsed with tap water to get rid of the attached soil and then all tree samples were rinsed 3 times with deionized water. Rinsed tree samples were oven-dried at 50 °C for 24 hours and ground to obtain a homogeneous powder with a metal-free mill. The soil samples were air-dried at
room temperature and then oven-dried at 50 °C for 48 hours. Dried samples were ground using a mortar and pestle and passed through a stainless steel sieve to obtain soil samples with grain sizes less than 2 mm. Ground samples of soil and trees were stored in sealed plastic bags until analysis. All soil and tree samples were analysed for heavy metals, i.e. Cu, Zn, and Cd, as well as metalloid As. Metal concentrations of Cd in soil and plant samples, as well as Cu and Zn in plant samples, were determined by graphite furnace atomic absorption spectrophotometer (GF-990, TAS-990). Metal concentrations of Cu and Zn in soil samples were determined by flame atomic absorption spectrophotometer (TAS-990). Soil sample digestion was conducted with nitric acid, hydrofluoric acid, and perchloric acid, while plant samples were digested with nitric acid (for Cd), or nitric acid and perchloric acid (for Cu and Zn). The content of As in soil and plant samples was determined by Nondispersive atomic fluorescence photometer (PF6-2), with the soil samples being digested with aqua regia and the plant samples being digested with nitric acid and perchloric acid. Soil pH was determined by pH meter, and the ratio of soil to water was 2.5:1. Soil organic matter, total nitrogen (TN), available phosphorus (P) and available potassium (K) were analysed with Potassium dichromate oxidation - external heating method, Kjeldahl method, Olsen method, and 1mol/L NH₄OAc (pH=7) extraction followed by flame spectrophotometry method, respectively.

2.4. Calculations and Data Treatment
Bio-concentration Factor (BCF) and Translocation Factor (TF) are the factors to determine the translocation ability of plants to accumulate heavy metals[1,14]. BCF was calculated as the ratio of the heavy metal/metalloid concentration in plant tissues to that in the soil i.e. BCF(%) = \( \frac{C_{\text{plant tissue}}}{C_{\text{soil}}} \), Where, \( C_{\text{plant tissue}} \) =concentration of heavy metal/metalloid in plant tissue (mg/kg) and \( C_{\text{soil}} \) =concentration of heavy metal/metalloid in the soil (mg/kg).

TF was calculated as the ratio of heavy metal/metalloid concentration in plant’s aerial part to that in plant root i.e. TF(%) = \( \frac{C_{\text{aerial part}}}{C_{\text{root}}} \), Where, \( C_{\text{aerial part}} \) =concentration of heavy metal/metalloid in plant’s aerial part (mg/kg) and \( C_{\text{root}} \) =concentration of heavy metal/metalloid in plant’s root (mg/kg).

All data calculation and tables making were performed in Excel 2010 and figures were drawn using GraphPad Prism 7 and Origin Pro2017.

3. Results and Discussion
3.1. Metals and Metalloids in the Soil
The soil of the study area is yellow-brown soil. The pH value was about 6.5. The average values of organic matter, TN, available P, and available K were about 9.1 g/kg, 0.85 g/kg, 7.9 mg/kg, and 71.6 mg/kg, respectively, belonging to the category of medium and low nutrition level. The contents of the four elements in the soil of the two sampling sites were presented in table 1, along with the background values of the elements in this region[15] as well as the risk screening and risk intervention values for soil contamination of agricultural land[16].

| Location or items | Cu (mg/kg) | Zn (mg/kg) | Cd (mg/kg) | As (mg/kg) |
|------------------|------------|------------|------------|------------|
| A                | 167.92     | 686.01     | 9.85       | 116.27     |
| B                | 216.01     | 684.09     | 11.73      | 118.70     |
| Background values in the region[15] | 20.40 | 62.00 | 0.097 | 9.00 |
| Risk screening values[16] | 100.00 | 250.00 | 0.30 | 30.00 |
| Risk intervention values[16] | / | / | 3.00 | 120.00 |

The risk screening value in the standard refers to the content of a pollutant in the soil of agricultural land, by which it is supposed to have a low risk to the quality and safety of agricultural products, the growth of crops or the ecological environment of soil, and the risk can be ignored under normal circumstances if a soil contains the pollutant equal to or lower than this value[16]. But if the value is
exceeded, there may be risks to the quality and safety of agricultural products, the growth of crops or the ecological environment of soil. The risk intervention value refers to the content of a pollutant in the soil of agricultural land, by which the edible agricultural products do not meet the quality and safety standards, and the risk of soil pollution in agricultural land is high if pollutant content exceeds this value\textsuperscript{[16]}. In principle, strict control measures should be taken in this case. Table 1 demonstrated that the contents of the four elements in the soil at both sites were much higher than the background values, with Cd being more than 100 times the background value and nearly 10 times for the other three elements. They were all higher than the risk screening levels, with Cd being 30 to 40 times that level and 1.7 to 4.0 times for the other three elements. The contents of Cd in the soil were even 3 to 4 times higher than the risk intervention level. As contents were just slightly lower than that level. So, it can be concluded that the soil in the study sites was seriously polluted by Cd. The second serious element was As. So, the soil is no longer suitable for agricultural use. With these high levels of toxic elements in the soil, especially of Cd and As, both species of trees grew well, demonstrating a high tolerance to these elements.

3.2. Metal and Metalloid Content in Different Parts of Poplar and Willow

Contents of the four elements in the root, bark, trunk, and branch of each tree and average levels of each tree species were demonstrated in table 2.

| Metal/metalloid | Tree\textsuperscript{a} | Heavy metal content (mg/kg) | Root | Bark | Trunk | Branch | Average |
|-----------------|------------------------|----------------------------|------|------|-------|--------|---------|
| P1              | 40.08                  | 28.19                      | 22.76| 28.37| 29.85 |
| P2              | 50.36                  | 49.44                      | 18.77| 17.69| 34.06 |
| Cu              | 45.22                  | 38.81                      | 20.76| 23.03| 31.96 |
| Avg_P           | 24.15                  | 30.06                      | 18.50| 16.69| 22.35 |
| W1              | 24.70                  | 52.39                      | 17.84| 17.33| 28.06 |
| W2              | 24.42                  | 41.23                      | 18.17| 17.01| 25.21 |
| Zn              | 130.85                 | 159.04                     | 71.38| 92.68| 113.49|
| Avg_P           | 24.12                  | 237.84                     | 76.31| 80.02| 141.37|
| W1              | 24.70                  | 341.52                     | 34.05| 25.37| 122.63|
| W2              | 151.07                 | 198.44                     | 73.85| 86.35| 127.43|
| Avg_W           | 24.42                  | 240.55                     | 29.37| 28.63| 94.86 |
| Cd              | 2.10                   | 1.08                       | 0.71 | 0.88 | 1.19  |
| Avg_P           | 2.14                   | 1.38                       | 0.69 | 0.81 | 1.25  |
| W1              | 0.53                   | 0.84                       | 0.17 | 0.20 | 0.44  |
| W2              | 0.27                   | 1.59                       | 0.30 | 0.24 | 0.60  |
| Avg_W           | 0.40                   | 1.22                       | 0.24 | 0.22 | 0.52  |
| As              | 8.40                   | 1.46                       | 0.24 | 0.55 | 2.66  |
| Avg_P           | 7.46                   | 1.65                       | 0.23 | 0.45 | 2.45  |
| W1              | 0.77                   | 2.16                       | 0.18 | 0.25 | 0.84  |
| W2              | 0.85                   | 4.63                       | 0.15 | 0.21 | 1.46  |
| Avg_W           | 0.81                   | 3.39                       | 0.17 | 0.23 | 1.15  |

\textsuperscript{a}P1=poplar 1; P2=poplar 2; Avg P=average values of poplar 1 and poplar 2; W1=willow 1; W2=willow 2; Avg W=average values of willow 1 and willow 2

The contents of the four elements varied among the parts and the species (table 2). On average, the concentration of Zn was the highest, followed by Cu. Contents of Cd and As were much lower than that of Zn and Cu for both poplar and willow. This might be because that Zn and Cu are less toxic for
plants and that higher amounts of the two elements existed in the soil (table 1). Each species presented higher content of As in the roots and barks than Cd, which might be due to much higher concentrations of As in the soil than Cd (table 1). In this study, heavy metal and metalloid contents in various parts of poplar were generally higher than the relative parts of willow, with the exception of the bark for Cu, Zn and As (table 2). This result was in contrast to the findings of Robinson et.al., who concluded that willow accumulated more Cd than poplar [9]. But commonly considerable variability of metal accumulation exists under various conditions [9].

For both poplar and willow, the contents of the four elements in the root and bark were higher than that in the trunk and branch (table 2). Between root and bark, element contents in the root of poplar generally exceeded that in the bark except Zn, while the contents were higher in the bark than that in the root for willow. Between trunk and branch, element contents in the branches generally surpassed that in the trunks for poplar, while the contents in the trunk exceeded that in the branch for willow except As. Thus, element contents in different parts of poplar were as follows Root>Bark>Branch>Trunk, except Zn, for which the bark had a higher concentration than the root. While for willow, the heavy metal and metalloid contents of different parts demonstrated a pattern as follows Bark>Root>Trunk>Branch, except As, for which the branch had higher concentrations than the trunk. The accumulation patterns with the importance of root and the differences in element allocation between poplar and willow were similar to other studies [8,17].

3.3. Phytoextraction Ability of Poplar and Willow

BCF manifests the transfer ability of heavy metals and metalloids from soil to various parts in the plant. In this study, BCFs of the four elements in the root, bark, trunk, and branch were calculated for poplar and willow based on the content data of soil and tree samples. The results were demonstrated in figure 1.

Figure 1. BCFs of heavy metal and metalloid elements for different parts of poplar and willow.
The BCFs of the different parts of the two species were in the range between 0.001 and 0.5 (figure 1), relatively low compared with some hyperaccumulator plants \cite{11,14}. With rather high As content in the soil and very limited uptake in trees, As demonstrated the lowest BCFs for each part for both poplar and willow, varying between 0.001 and 0.072 (figure 1 (d)). On average, Cd presented slightly lower BCFs than Cu and Zn for the two tree species, which might be due to higher toxicity of Cd for trees than the other two elements. BCFs of the four elements in the root, trunk, and branch of poplar were higher than that of willow. But willow generally presented higher BCFs in the bark than that of poplar, especially for Zn and As.

Like the content distribution in various parts, the BCFs of the bark and root were also higher than that of the trunk and branch for the two tree species. For poplar, BCFs of the root were higher than that of the bark, with the exception of Zn. While for willow, BCFs of the bark exceeded that of the root for all four elements. The BCFs of the branch and the trunk for each tree, as well as for each species, were at a similar level, with that of the branch being only slightly higher than the trunk in general.

TF manifests the ability of further transportation of heavy metals and metalloids from root to aerial parts in the plant. TFs of the four elements in the bark, trunk, and branch were calculated for poplar and willow and demonstrated in figure 2.

The TFs in this study were in the range between 0.03 and 5.81 (figure 2). On average, poplar presented lower TFs than willow, with the exception of Zn in the trunk and branch. TFs of the bark were higher than that of the trunk and branch for both species. TFs of the branch were slightly higher than that of the trunk for all four elements for poplar. While the TFs of the branch and trunk varied among trees and elements for willow. TFs of the four elements for poplar and willow were as follows Zn>Cu>Cd>As and Cd>As>Zn>Cu, respectively. TFs greater than 1 existed mainly for all elements in the bark of willow as well as for Zn in the bark of poplar.
3.4. Remediation of the Soil with Poplar and Willow

The soil of the study sites has been polluted with heavy metals and metalloids, especially with Cd and As. The land is no longer suitable for agricultural use. Dendroremediation with local tree species such as poplar and willow is a practical technology for the recovery of the soil with the following considerations. First, both species have a strong tolerance to the toxic elements[11]. Second, they are fast-growing species with high biomass, which can grow on nutrient-poor soil. Even though the BCFs for the elements do not attain the hyperaccumulation levels[1,14], considerate amounts of toxic elements could be removed[9]. Thirdly, trees have a deep root system, which will extract elements from the lower part of the soil. Besides, forestation has a comprehensive effect not only on the environment but also on ecosystem recovery. Fast-growing wood can be harvested as by-products to have extra economic benefits[9]. Since both species are not hyperaccumulators of the toxic elements, especially for As, it is suggested to apply forestation intercropped with grass or herbs with the super cumulative capacity of toxic elements[14]. In doing so, further study should be carried out in the technology of forest culture and management, as well as forest intercropping technology.

In dendroremediation practice, heavy metals and metalloids are expected to be accumulated in the aerial part, especially the stem. In this study, bark demonstrated relatively high phytoextraction ability both in BCF and TF. But the trunk, where most of the biomass of a tree is, had usually the lowest phytoextraction ability. Further research might also focus on promoting the phytoextraction ability of the tree species, especially in trunk.

4. Conclusion

The soil of the study sites in the floodplain district downstream the mining hill in Tongling city was polluted in terms of Cu, Zn, Cd, and As, with Cd being the most critical element which greatly violated the risk intervention standard for soil contamination of agricultural land. In spite of this, poplar and willow trees grew well under the stress. Both species demonstrated certain phytoextraction abilities of these elements, with BCFs of different parts of the trees being between 0.001 and 0.5. Zn and Cu demonstrated the highest averaged BCFs among the four elements for both tree species, then followed by Cd. Both species had a rather low accumulation of As. Poplar showed relatively higher averaged BCF than willow except As, while willow had higher averaged TF than poplar. The root and bark absorbed more these elements than the trunk and branch, also demonstrating higher BCFs. And the bark had higher TF than trunk and branch.

Both species are not hyperaccumulators of the studied elements. Nevertheless, they are suitable for the soil remediation and forestation in this region when their tolerance to heavy metals and metalloids, their phytoextraction ability, as well as ecological effects are all taken into consideration.

Acknowledgments

The authors are pleased to acknowledge the financial support provided by 2017-2021 National Science Foundation of China “Study on the mechanism of formation of heavy metal accumulated wood in controlled plantation Poplar. Project No. 31770595”.

References

[1] Ali H., Khan E., Sajad M.A. 2013. Phytoremediation of heavy metals--concepts and applications. Chemosphere, 91(7), 869-881.
[2] Chen J., Yang Z., Su Y., Han F.X., Monts D.L. 2009. Phytoremediation of heavy metal/metalloid-contaminated soils. in: Contaminated Soils: Environmental Impact, Disposal and Treatment. (Ed.) R.V. Steinberg, Nova Science Publishers, Inc.
[3] Mahar A., Wang P., Ali A., Awasthi M.K., Lahori A.H., Wang Q., Li R., Zhang Z. 2016. Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: a review. Ecotoxicology and environmental safety, 126, 111-121.
[4] Escarré J., Lefèbvre,C., Raboyeau S., Dossantos A., Gruber W., Marel J.C.C., Frérot H., Noret N., Mahieu S., Collin C. 2011. Heavy metal concentration survey in soils and plants of the Les Malines mining district (Southern France): implications for soil restoration. Water, Air, & Soil Pollution, 216(1-4), 485-504.
[5] Martin C.W. 2000. Heavy metal trends in floodplain sediments and valley fill, River Lahn, Germany. Catena, 39(1), 53-68.

[6] Wang W., Sun L. 2016. Coupled Analysis Regional Innovation System and Resource City Industrial Transformation: A Case Study of Tongling City. Scientia Geographica Sinica, 36(2), 204-212. (In Chinese)

[7] Wang Y.C., Wang Y., Wu X.Q., Ren KX, Zhou J. 2010. Evaluation on sustainable development of mineral resources cities -- a case study of tongling city in anhui province. Coal Economic Rese (9), 35-40+59. (In Chinese)

[8] Gonzalez-Oreja J.A., Rozas M.A., Alkorta I., Garbisu C. 2008. Dendroremediation of Heavy Metal Polluted Soils. Rev Environ Health. 23(3), 1-12.

[9] Azzarello E., Pandolfi C., Pollastri S., Masi E., Mugnai S., Mancuso S. 2011. The use of trees in phytoremediation. Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources, 6(37), 1-15.

[10] Langholtz M., Carter D.R., Rockwood D.L., Alavalapati J.R., Green A. 2005. Effect of dendroremediation incentives on the profitability of short-rotation woody cropping of Eucalyptus grandis. Forest Policy and Economics, 7(5), 806-817.

[11] Dickinson N. 2000. Strategies for sustainable woodland on contaminated soils. Chemosphere, 41(1-2), 259-263.

[12] Alahabadi A., Ehrampoush M.H., Miri M., Aval H.E., Yousefzadeh S., Ghaffari H.R., Ahmadi E., Talebi P., Fathabadi Z.A., Babai F. 2017. A comparative study on capability of different tree species in accumulating heavy metals from soil and ambient air. Chemosphere, 172, 459-467.

[13] Lin Q.X. 2016. Analysis on Climatic Characteristics and Changes of Tongling Area During 1960 to 2012. Modern Agricultural Science and Technology (9), 238-240. (In Chinese)

[14] Van der Ent A., Baker A.J., Reeves R.D., Pollard A.J., Schat H. 2013. Hyperaccumulators of metal and metalloid trace elements: facts and fiction. Plant and Soil, 362(1-2), 319-334.

[15] Centre C.N.E.M. 1990. Background values of soil elements in China, China Environmental Science Press, Beijing, China.

[16] Ministry of Ecological Environment, PRC. 2018. Soil environmental quality risk control standard for soil contamination of agricultural land. National standard of the People’s Republic of China. (GB15618-2018).

[17] Pilipovića A., Zalesny R.S., Rončević S., Nikolić N., Orlović S., Beljin J., Katanić M. 2019. Growth, physiology, and phytoextraction potential of poplar and willow established in soils amended with heavy-metal contaminated, dredged river sediments. Journal of Environmental Management, 239, 352-365.