CHEMICAL ENGINEERING TRANSACTIONS
VOL. 59, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216

DOI: 10.3303/CET1759149

Environmental Chemistry Study on Spatial Variability of Heavy Metal in Crops in Funiu Mountain Area

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In this paper, we take Funiu Mountain area as the target area, and collect forsythia and soil samples there and conduct environmental chemistry study on the spatial variability of heavy metal in forsythia grains in this area. The results show that the content of heavy metal in forsythia grains in most part of the area is lower than the national food hygiene standard, but in some surrounding areas of factories, the Cd content exceeds the standard. The Cu, Pb and Cd contents in soil have significant impacts on the contents and enrichment of the three heavy metal elements in forsythia. By using multiple linear regression, we obtain the prediction model for heavy metal content in forsythia. This model is of great statistical significance and can provide reference for the management of wild medicinal materials and the quality and safety control of wild medicinal products in Funiu Mountain area.

1. Introduction

Heavy metal is difficult to degrade and migrate. Once it enters the soil, it becomes a permanent pollutant accumulating in the soil and it is very difficult to remove (Farooq et al., 2010; Oncel et al., 2000; Hooda and Alloway, 1996; Mandal, 2016; Srisorrachatr, 2017; Santana et al., 2017; Duplancic et al., 2017). Crops are the primary producers in the food chain. Excessive heavy metals accumulated in their roots, stems, leaves and fruits not only seriously interfere with the growth of the crops, but also affect the quality of wild medicinal products and ultimately threatening the health of animals and human through the food chain (Lavado et al., 2001; Bounaouara et al., 2015; Mortvedt et al., 1981). Therefore, it is necessary to further study the relationship between the content of heavy metal in the soil and that in the crops growing there and summarize the migration and transformation patterns of heavy metals in the soil-plant system under natural conditions.
In this paper, we take Funiu Mountain area as the target area, and collect forsythia and soil samples there and conduct environmental chemistry study on the spatial variability of three heavy metal elements - Cu, Pb and Cd in forsythia grains in this area (Bermudez et al., 2011; Lv and Feng, 2015; Karami et al., 2009).

2. Testing method

2.1 Sample collection

We collect 98 forsythia samples, of which 67 are from cambisols and 31 from anthrosols; 52 are from farms and 46 from the surrounding areas of factories of different kinds. Within an area of 600m^2 around each sampling site, we collect forsythia grains from 4~5 points, mix them well and then put them into bags.
Sampling points for soil are consistent with those of forsythia. Soil samples are collected from the plough layer (0~15cm).

2.2 Sample analysis

We wash and dry the forsythia grain samples, crush and sieve them and place them in sealed sample sacks for later use. We adopt the HNO3-HClO4 resolution method: weigh 1.0g of crop sample and place it into a 150ml Erlenmeyer flask, add 15ml of HNO_3 GR; after overnight digestion, heat it for digestion until only 2ml of the solution is colorless and transparent. After that, use 1%HNO3 to wash it into the 25ml volumetric flask to volume (Sovrani et al., 2012; Cui and Du, 2011).

For soil samples, we use Lefort aqua regia digestion method: place 0.5~1.0g of soil sample (100 mesh) in a polytetrafluoroethylene crucible, add 6~12 ml of Lefort aqua regia (nitric acid/hydrochloric acid = 3/1), shake it and let it sit overnight. The next day, let it digest for 4~5h at a temperature of 100~170°C, and then heat it (do not boil it) until only about 1ml of the digestive solution is left. After cooling it to room temperature, use 1% nitric acid to dissolve the residue and filter and transfer it to a 25 ml volumetric flask to volume (Saad et al., 2006).

The content of Cd in soil and forsythia is determined by the graphite furance atomic absorption spectrometry and the contents of Cu and Pb by the flame atomic absorption spectrometry (Umar et al., 2010).

2.3 Data processing method

We use SPSS (13.0) software for variance analysis, conduct Duncan test to compare the differences in the contents of heavy metals; and adopt the multiple linear regression analysis to build the heavy metal accumulation model for forsythia.

The evaluation on the heavy metal in crops mainly refers to national food hygiene standards: Cu-10mg/kg (GB15199-1994), Pb-0.2μg/kg (GB2762-2005) and Cd-0.2μg/kg (GB2762-2005).

3. Heavy metal content in forsythia and its spatial variability

3.1 Statistical analysis on heavy metal in forsythia and pollution evaluation

Frequency charts for contents of heavy metal elements in forsythia in Funiu Mountain area are shown in Figure 1.

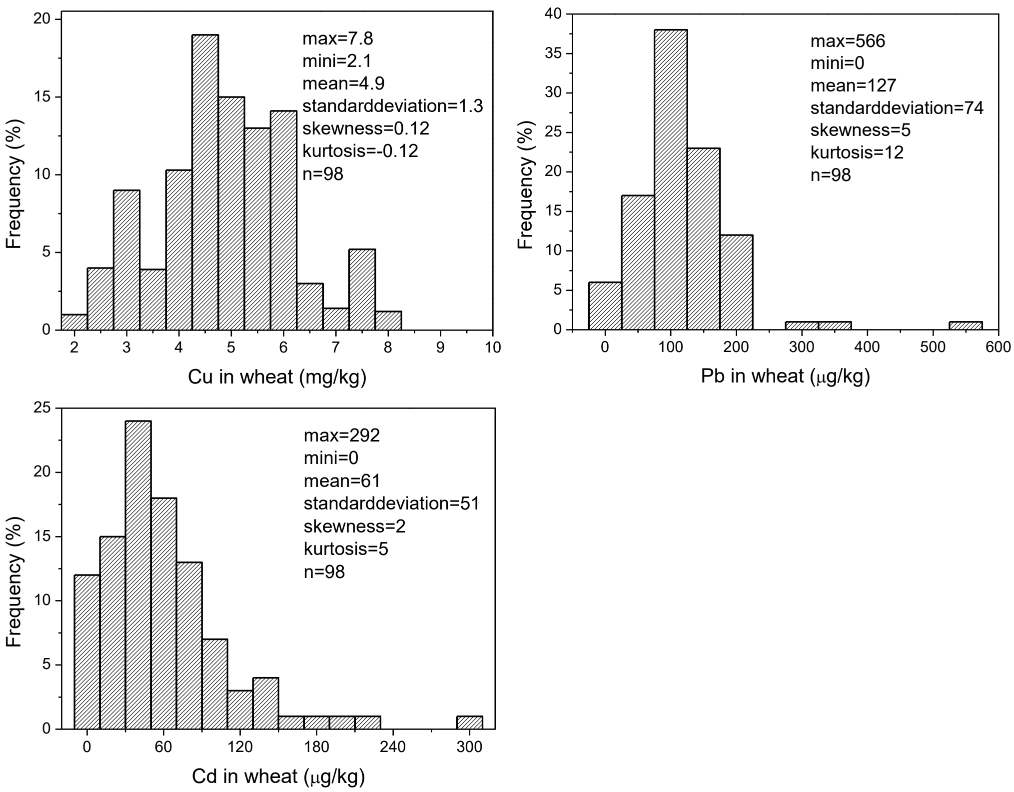

Figure 1: Frequency distribution of three heavy metals in forsythia

It can be seen from the figure that, the average content of Cu in forsythia is 4.9mg/kg and that the contents of Cu in all samples are<10mg/kg, which are in line with *National Food Hygiene Standards*. The average content of Pb is 127μg/kg, which is lower than the limit, but in 8.2% of the samples, the content of Pb exceeds the standard. The average content of Cd is 67μg / kg, lower than the limit, but the content of Cd in 3 forsythia samples exceeds the standard. Therefore, currently, there is no health risk caused by heavy metal Cu in the forsythia in Funiu Mountain area, while in some forsythia grains, there are accumulation of the heavy metals Pb and Cd, which may affect the health of human bodies and should cause people’s attention.

From Figure 1, it can also be seen that the contents of Cu and Cd show normal distributions, indicating that there is no abnormal accumulation of Cu and Cd in forsythia; while the content of Pb in forsythia shows a non-normal distribution and is right-skewed, indicating that it may have been affected by some abnormal factors, making the content of Pb at some sampling points abnormal.

3.2 Changes in contents of heavy metals in forsythia on different types of soil

Table 1 lists the contents of heavy metal elements in forsythia grains on different types of soil.

Table 1: Heavy metal contents in forsythia grains on different soils

Soil	Cu (mg/kg)	Pb (μg/kg)	Cd (μg/kg)
Cambisols (67)	4.8±1.2a	128±85a	48±45b
Anthrosols (31)	5.0±1.3a	125±46a	87±52a

The different letters following each average value indicate the significant difference when p=0.05.
From the table, we can see that the contents of Cu and Pb on cambisols and anthrosols are close. Variance analysis indicates that, the content of Cd in forsythia on different types of soils is significantly different ($p<0.01$). The content of Cd in forsythia on cambisols is obviously lower than that on anthrosols. This probably has something to do with the soil Eh, because Cd is a reduced refractory element.

3.3 Variations in the contents of heavy metals in forsythia in the surrounding areas of factories

Table 2 lists the contents of heavy metals in forsythia in the surrounding areas of different kinds of factors.

Table 2: The heavy metal contents of forsythia around different types of factories

Company type	Cu (mg/kg)	Pb (μg/kg)	Cd (μg/kg)
Chemical industry	5.1±1.5a	129±77ab	98±63a
Metallurgy industry	4.6±1.4ab	182±230a	45±14b
Breeding industry	4.1±1.1ab	107±49b	62±35ab
Textile industry	3.8±1.4b	156±38ab	96±34a
Factory	4.7±1.4A	132±94A	80±54A
soil	5.0±1.1abA	122±52abA	43±41bB

The lowercase letter following each average value indicates the significant difference when p=0.10, and the uppercase letter following each average value indicates the significant difference when p=0.05. From the table we can see that, there is not much change in the contents of Cu and Pb in forsythia samples collected from farms, while the content of Cd in forsythia in the surrounding areas of factories is much greater than that on farms ($p<0.01$). From the same type of heavy metal, after comparing the content in the forsythia grains around different types of factories, we find that the contents of Cu and Cd in the forsythia around chemical factories are higher than those around other ones; and the content of Pb in the forsythia around metallurgical factories is the highest. These features are quite similar to the enrichment of these heavy metals in the soil.

3.4 Impacts of heavy metal contents in the soil and soil properties on the accumulation of heavy metals in forsythia

The relationships between the contents and bio-concentration factors of heavy metals in forsythia and (BCF) and the total content of heavy metals in the soil and the soil properties are shown in Table 3.
The descriptive statistics of the bio-concentration factor (BCF) of heavy metal in forsythia are listed in Table 4.
Studies have shown that soil properties have significant effects on the accumulation of heavy metals in crops (Jing et al., 2016; Zaccone et al., 2010). From the stepwise linear regression relationships between the content of heavy metal in forsythia and the total content of heavy metals in the soil and soil properties (pH and SOM), we can see that the content of Cu in forsythia has a positive correlation with the total content of heavy metals in the soil, but that it also has a positive correlation with the soil SOM. The content of Pb in forsythia is only positively correlated with the total content of Pb in the soil; in addition, the content of Cd in forsythia is positively correlated with the total content of CD in the soil and SOM and negatively correlated with the pH value of the soil.
We use the bio-concentration factor (BCF), that is, the heavy metal content in forsythia grains divided by the heavy metal content in the soil. We also conduct stepwise linear regression analysis on the bio-concentration factor of each element and the total content of heavy metal in the soil and soil properties. From the results, it can be seen that the total content of Cu in the soil is positively correlated with Cu in forsythia and negatively

correlated with BCF-Cu, which indicates that the total content of heavy metal in the soil has an important effect on the content and enrichment of Cu in forsythia. The content of Cu in forsythia is positively correlated with SOM, and BCF-Cu is negatively correlated with soil pH value, which indicates that soil properties have some effects on the content of Cu in forsythia and BCF-Cu, and changes in the soil pH value and SOM can lead to the changes in the bio-availability of Cu in the soil.

The content of Pb in forsythia is positively correlated with the content of Pb in the soil, and BCF-Pb is negatively correlated with the content of Pb in the soil, which indicates that the accumulation f Pb in forsythia is closely related to the total content of Pb in the soil, that the content of Pb in the soil may be just one of the important sources for Pb in forsythia, and that the absorption of Pb in forsythia is greatly affected by human activities, such as car roads. The particles containing Pb floating in the air are absorbed by the surface of the forsythia, contaminating the agricultural products.

The content of Cd in forsythia is positively correlated with the content of Cd in the soil, and BCF-Cd is negatively correlated with the content of Cd in the soil, and at the same time, the content of Cd in forsythia and BCF-Cd are negatively correlated with the pH value of soil. All these indicate that the total content of Cd in the soil and the soil pH value significantly affect the content and enrichment of Cd in forsythia and that Cd has high availability in the soil and that its availability is affected by the soil pH value. At the same time, compared with Cu and Pb, Cd can be more easily accumulated in forsythia.

Table 3: Relationship between heavy metal contents, BCF and the soil characters and the total contents of the heavy metal in soil

Dependent variable	Independent variable	Partial regression coefficient	Standard error	Standard partial coefficient	P
Cu in forsythia (98)	Con	3.069	0.655		R=0.276*
	SOM	0.045	0.022	0.206	
	Cu in soil	0.027	0.016	0.169	
Lg[10 (Pb in forsythia) +1] (98)	Con	0.272	0.028		R=0.254*
	Pb in soil	0.002	0.001	0.254	
Cd in forsythia (98)	Con	0.196	0.051		R=0.691**
	pH	-0.027	0.005	-0.463	
	Cd in soil	0.159	0.023	0.535	
	SOM	0.001	0.001	0.153	
BCF-Cu (98)	Con	33.853	3.743		R=0.571**
	Cu in soil	-0.329	0.055	-0.511	
	pH	-0.986	0.493	-0.172	
BCF-Cu (98)	Con	0.241	0.032		R=0.335**
	Pb in soil	-0.001	0	-0.287	
	SOM	-0.002	0.001	-0.179	
BCF-Cu (98)	Con	3.345	0.232		R=0.648**
	pH	-0.223	0.032	-0.563	
	Cd in soil	-0.455	0.165	-0.221	

Table 4: Bio-concentration factors (BCF) of heavy metals in forsythia grains

	Mini	Max	Average	Standard deviation
BCF-Cu (98)	6.01	29.37	16.30	5.07
BCF-Cu (98)	0.00	2.47	0.43	0.30
BCF-Cu (98)	0.00	563.40	45.78	66.30

4. Statistical model for accumulation of heavy metals in forsythia grains

4.1 General form of the model

The content of heavy metal in forsythia grains is affected by soil properties such as pH, SOM and total content of heavy metal in the soil. In order to further study the quantitative relationship between the content of heavy metal in forsythia grains and its influencing factors, we adopt the stepwise regression analysis to obtain a statistical model for the content of heavy metal in forsythia grains and summarize the data in Table 3 as follows:

$$Cu_w = 3.069 + 0.272 \times Cu_T + 0.045 \times SOM \tag{1}$$

$$Lg(10Pb_W + 1) = 0.272 + 0.002 \times Pb_T \tag{2}$$

$$Cd_W = 0.196 + 0.159 \times Cd_T - 0.027 \times pH + 0.01 \times SOM \tag{3}$$

Cu, Pb and Cd represent the contents of Cu, Pb and Cd, and the subscripts w and T stand for forsythia and soil; Cu_T, Pb_T and Cd_T represent the total contents of the three heavy metals in the soil, in mg/kg; SOM is the content of organic matters in the soil, in g/kg; and pH is the pH value of the soil.

4.2 Regression analysis on the model

Through the back substitution calculation, we obtain the predicted value of the model, and then objectively analyze the model with the variation trends of the predicted value and the measured value. We substitute the test data into Equations (1), (2) and (3), respectively, and obtain the predicted values of the contents of the three heavy metals Cu, Pb and Cd in forsythia grains, where the content of Pb in forsythia is expressed in the logarithmic form.

4.3 Model validation

Here we introduce the non-linear model. We take the content of Cd in forsythia grains as an example to validate the simulation effect of the content of heavy metal in forsythia in Funiu Mountain area. The model for the accumulation of Cd in forsythia grains is as follows:

$$Cd_P = 0.560 \times EXP[\,0.995 \times \log(Cd_T) - 0.173 \times pH + 0.018 \times SOM] \tag{4}$$

We substitute the total contents of Cd, pH and SOM in the soil obtain from the experimental analysis into Equation (4) and obtain the calculated value of Cd in forsythia grains.

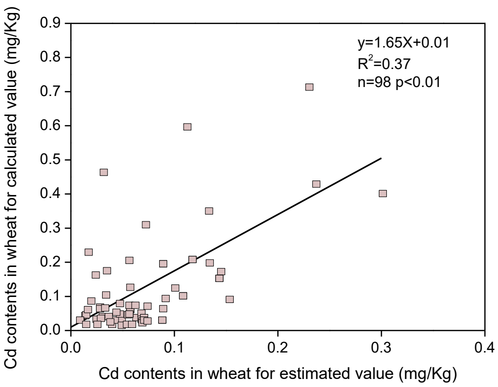

Figure 2: Correlation of computed with measured Cd content in forsythia grains

From Figure 2, it can be seen that, the value calculated from Equation (4) is well correlated with the measured value-Y=1.65X+0.01 (R=0.37, P<0.001, n=98), indicating that this model can be applied to predict the content of Cd in forsythia so as to provide reference for the agricultural management and the quality and safety control of agricultural products in Funiu Mountain area.

5. Conclusions

In this paper, we collect soil and forsythia samples in the surrounding areas of farms and factories and conduct environmental chemistry study on the spatial variability of three heavy metal elements - Cu, Pb and Cd in forsythia grains in Funiu Mountain area. The main conclusions are as follows:

1. The content of heavy metal in forsythia grains in most part of the area is lower than the national food hygiene standard, but few Cd samples exceed the standard, which are mainly from the surrounding areas of factories. In the surrounding areas of chemical enterprises, the contents of Cu and Cd in forsythia are obviously higher, which is consistent with the enrichment of heavy metals in the soil to some extent.
2. The Cu, Pb and Cd contents in soil have significant impacts on the contents and enrichment of the three heavy metal elements in forsythia.
3. By using multiple linear regression, we obtain the prediction model for heavy metal content in forsythia. This model is of great statistical significance and can provide reference for the management of wild medicinal materials and the quality and safety control of wild medicinal products in Funiu Mountain area.

Acknowledgments

This paper is supported by Soft science research plan project (No. 162400410119) in Henan province.

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