Investigation of Heavy Metal Cd, Pb and Cr in Andisols as Affected by the Amelioration of Steel Slag and Rice Husk Bokashi

Rina Devnita, Mahfud Arifin, Apong Sandrawati, Rija Sudirja
Soil Science Department, Faculty of Agriculture, Universitas Padjadjaran
Jl Raya Bandung-Sumedang km 21 Jatinangor 45363
Corresponding author: rina.devnita@unpad.ac.id

ABSTRACT

The application of steel slag and bokashi of husk in Andisols has been acknowledged to decrease P-retention and increase available P. However, steel slag contains heavy metals that may harm soils. The objective of this research was to find out the effect of amelioration steel slag and bokashi of husk in Andisols on the heavy metals contents (Cd, Pb and Cr) in the soil. The treatments were arranged in randomized block designed in factorial pattern with two factors: steel slag and bokashi of husk, each consisted of four level: 0, 2.5, 5.0 and 7.5 % in 10 kg soil weight (w/w), thus the total was 16 combined treatments and repeated three times. The treatments were incubated for four months and then the P-retention, available P, Cd, Pb and Cr contents in the soil were analyzed. The results showed that steel slag and bokashi of husk interacted in decreasing 6.67% of P-retention and increasing 60 ppm of available P. This research also informed that Cd, Pb and Cr contents in the soil after the treatments were still lower than the critical value that were permitted.

Keywords: heavy metals, P-retention, available P, critical value.

1. INTRODUCTION

Andisols have a high potential for agriculture production. Although, there are many problems with nutrient management in Andisols. Amelioration of Andisols is intended to decrease P-retention and increase available P (Qafoku, 2004). Silicates and organic matter can be used as ameliorant in Andisols due to their high negative charge which can block the soil positive charges, thus decreasing P-retention and increasing available P.

Steel slag is a by-product of steel making. The slag is a complex solution of silicate that come from furnace process, and its no longer used. Bokashi known as East Asia origin concept of composting. Bokashi produced from any kind of organic matter with fermented process (Higa, 1991). The most important is, there are certain bacteria added during fermented process.

Steel slag with bokashi of rice husk that act as organic matter are ameliorants used in Andisols. However, the heavy metals contents in steel slag need to be considered due to their negative effects on soils and plants. Treatments to the soil have to cover not only the main objectives, but also the side effect that accompanied of such a process.

Steel slag is the by-product of steel industries. This material contains silicates that can increase soil negative charges. It also comprises calcium and magnesium that can function as a lime. Japan, United State and Germany are some countries that use steel slag to increase soil pH (Ma et al., 1989). However, some components also accompany the steel slag, and it needs more detailed study related to their aspect to soil quality. There are some heavy metals in steel slag like Pb, Cr, and Cd (Navarro et al, 2010), which are considered as dangerous and poisonous materials. Application of steel slag into the soils can be interpreted as giving the poisonous and dangerous materials to the soils.

Therefore, this research aims to study the influence of steel slag and bokashi of rice husk to improve Andisols characteristics. The most importance is to reduce P retention and improve P available. In the other hand, the heavy metals contents in soils as effected by steel slag added, need to considered and analyzed.
2. METHODS

The soils for this research were sampled compositely from several points of 0-20 cm depth in Andisols derived from Mt. Tangkuban Parahu in Lembang, West Java. The samples were incubated with steel slag and bokashi of husk. The steel slag was obtained from PT. Krakatau Steel Indonesia. Bokashi of husk were made by adding the EM4 microorganisms to the husk and fermented for four weeks before using as ameliorants. Prior to the treatments, some physical and chemical properties of the soil samples and bokashi of husk were analyzed such as organic C, Al + ½ Fe extracted by acid ammonium oxalate, pH, available P, cation exchange capacity according to Van Reeuwijk (2002), P-retention (Blakemore et al., 1987), bulk density (Bielders et al., 1990) and heavy metals (Cd, Pb and Cr) contents.

Randomized Block Designed was used as experimental design in this research. It was a factorial with two factors, and each factor consisted of four levels. The first factor was steel slag and the second factor was bokashi of husk. Four levels 0, 2.5, 5.0 and 7.5% of soil on weight/weight (w/w) were applied for both steel slag ad bokashi of husk. The combined treatments were 16, repeated three times which was placed in 48 polybags. The size of steel slag was uniform, passed the sieve of 200 mesh. Incubation was done by adding the steel slag and bokashi of husk according to the treatments to the soils (10 kg) and kept for four months. After incubation periods, some parameters such as P-retention, available P, and heavy metals Cd, Pb and Cr contents were analyzed.

3. RESULT AND DISCUSSION

3.1 Data of Soil, Steel Slag and Bokashi of Rice Husk

The location of soil sampling was in Lembang, Bandung Regency District West Java Province Indonesia, in several points around the coordinate of 107°38’57.0” S - 06°47’07.7”. The areas have Andisols soils developed from the eruption materials of Mt. Dano and Mt. Tangkuban Parahu (Silitonga, 2003) which consisted of andesitic brownish sandy tuffs, very coarse hornblend crystals and red weathered andesitic brownish sandy tuffs, red weathered lahar, lapilli layers and breccia (reference). The sampling areas had slope of 8%.

The results of soil analyses prior to incubation are presented in Table 1. The data shown that the soils fulfilled the requirements of andic soil properties (Soil Survey Staff, 2014) to be classified as Andisols as the organic carbon was less than 25% (4.43%), bulk density was 0.9 g cm\(^{-3}\) or lower (0.9 g cm\(^{-3}\)), P-retention was more than 85% (88.86%) and Al + ½ Fe with ammonium oxalate was more than 2% (5%). The low available P (9.41 ppm) was due to the high P-retention (88.86%). The soil reaction was acid (5.49) and classified as medium CEC (2.63 cmol kg\(^{-1}\)) and medium base saturation (30.35%). The low bulk density (0.90%) was not only due to the high organic carbon content (4.43%) but also tuff parent materials.

```
Table 1 Some chemical, physical and biological characteristics of the soil

| No. | Parameters                                      | Unit   | Value  | Criteria\(^a\) |
|-----|------------------------------------------------|--------|--------|----------------|
| 1.  | Organic Carbon                                 | %      | 4.43   | High           |
| 2.  | Bulk density                                    | g cm\(^{-3}\) | 0.90   | low            |
| 3.  | P-retention                                    | %      | 88.86  | high           |
| 4.  | Al + ½ Fe with acid ammonium oxalate           | %      | 5.00   | high           |
| 5.  | Available P                                    | mg kg\(^{-1}\) | 9.41   | low            |
| 6.  | pH \(H_2O\)                                    | -      | 5.49   | acid           |
| 7.  | Cation Exchange Capacity (CEC)                 | cmol kg\(^{-1}\) | 22.62  | medium         |
```

\(^a\)Source: Buchholz et al. (2004)
Table 2 informs the result of steel slag and bokashi of husk analyses. The alkaline and netral pH of steel slag and bokashi husk (11.8 and 7.47) were expected to recover and increase the pH of Andisols. The medium and high CEC in steel slag and bokashi of husk (25.6 and 40.01 cmol kg\(^{-1}\)) were likely could increase the CEC of Andisols. In addition, the greater amount of SiO\(_2\) content in steel slag and bokashi of husk (12.5 and 60.6%) was intended to release some silicon ions that will replace the phosphate retained in the soils. The content of SiO\(_2\) in rice husk was 60.6 %, its lower than Coniwati et. al. (2008), which found that SiO\(_2\) in rice husk was 76.7%. The content of SiO\(_2\), would be depend on purify methods. Meanwhile, the bulk density in steel slag in contrary was very high (2.7 g cm\(^{-3}\)), but it was balanced by the very low bulk density of bokashi of husk (0.3 g cm\(^{-3}\)).

### Table 2: Some chemical and physical characteristics of steel slag and bokashi of rice husk

| No. | Parameters       | Unit       | Value  |
|-----|------------------|------------|--------|
| 1.  | pH H\(_2\)O      | -          | 11.8   |
| 2.  | Cation Exchange  | cmol kg\(^{-1}\) | 25.6  |
| 3.  | SiO\(_2\)        | %          | 12.50  |
| 4.  | CaO              | %          | 42.00  |
| 5.  | MgO              | %          | 6.00   |
| 6.  | P\(_2\)O\(_5\)   | %          | 0.50   |
| 7.  | FeO              | %          | 0.81   |
| 8.  | Water content    | %          | 1.00   |
| 9.  | Bulk density     | g cm\(^{-3}\) | 2.70  |
| 10. | Cd               | mg kg\(^{-1}\) | 0.42  |
| 11. | Pb               | mg kg\(^{-1}\) | trace |
| 12. | Cr               | mg kg\(^{-1}\) | 94.7  |
| Bokashi of husk |                      |           |        |
| 1.  | pH H\(_2\)O      | -          | 7.47   |
| 2.  | CEC              | cmol kg\(^{-1}\) | 40.01 |
| 3.  | SiO\(_2\)        | %          | 60.6   |
| 4.  | Organic carbon   | %          | 24.64  |
| 5.  | Total nitrogen   | %          | 1.37   |
| 6.  | C/N              | -          | 17.96  |
| 7.  | Bulk density     | g cm\(^{-3}\) | 0.3   |

3.2 P-retention and P available

Steel slag and bokashi of husk interacted in decreasing P retention and in increasing available P as reported in Table 3 and 4. The lowest values were found at 83.60% (5% steel slag and without bokashi) and 83.09% (7.5% steel slag and 7.5% bokashi of husk). These ameliorants decreased P retention about 6.67% compared to the control treatment. The decrease of P-retention was more eminent with steel slag than with bokashi of husk. Steel slag produces silicic anions with high affinity that are able to compete with phosphate in occupying the sites in non-crystalline minerals and may release some phosphate anions, decreasing the P-retention. This founding was in line with Qafoku et. al. (2004) which mentioned that P-retention can be decreased by the addition of silicate. The organic acids derived from the decomposition of bokashi of husk also contain carboxyl group that can also compete to replace the phosphate ions. However, the silicate anions were more distinctive in replacing them.

Steel slag and bokashi of husk interacted in increasing available P as shown in Table 4. The increase of available P was in accordance with the decrease of P-retention. The release of
retained P to the soil solution could add the amount of dissolved phosphate ions and increase available P. The increase of available P was due to not only the silicate in steel slag and organic acid in bokashi of husk, but also the high contents of Ca and Mg. Steel slag had 42 and 6% of CaO and MgO, respectively. The mineralization of steel slag also contributed Ca and Mg to soil solution. These cations functioned as lime and increased soil pH which then increase the concentration of OH⁻ ions. These ions can also substitute the phosphate ions and release them to soil solution, so more available P was detected as mentioned by Boniao (2000).

| Bokashi of Husk | Steel Slag | 0%       | 2.5%     | 5%       | 7.5%     |
|-----------------|------------|----------|----------|----------|----------|
| 0%              | 90.96 (b)  | 86.08 (ab)| 83.60 (a)| 85.10 (b)|          |
|                 | C          | B        | A        | AB       |          |
| 2.5%            | 92.16 (b)  | 86.85 (b)| 84.29 (ab)| 86.10 (b)|          |
|                 | C          | B        | A        | B        |          |
| 5%              | 86.83 (a)  | 85.19 (a)| 85.99 (bc)| 84.05 (ab)|          |
|                 | B          | AB       | B        | A        |          |
| 7.5%            | 95.40 (c)  | 92.16 (c)| 87.36 (c)| 83.09 (a)|          |
|                 | D          | C        | B        | A        |          |

Note: The letters in parentheses are read horizontally, the letters without parentheses are read vertically. The same letters indicate no difference values between the treatments and Duncan Multiple Range Test 5%.

| Bokashi of Husk | Steel Slag | 0%       | 2.5%     | 5%       | 7.5%     |
|-----------------|------------|----------|----------|----------|----------|
| 0%              | 10.02 (a)  | 57.87 (b)| 55.76 (a)| 56.21 (a)|          |
|                 | A          | B        | B        | B        |          |
| 2.5%            | 34.24 (b)  | 43.21 (a)| 65.51 (b)| 70.01 (c)|          |
|                 | A          | B        | C        | B        |          |
| 5%              | 48.95 (d)  | 57.34 (b)| 60.53 (ab)| 61.43 (ab)|          |
|                 | A          | B        | B        | B        |          |
| 7.5%            | 41.34 (c)  | 54.34 (b)| 58.18 (a)| 65.24 (bc)|          |
|                 | A          | B        | B        | C        |          |

Note: The letters in parentheses are read horizontally, the letters without parentheses are read vertically. The same letters indicate no difference values between the treatments and Duncan Multiple Range Test 5%.

The increase of available P in this research was parallel with the higher amount of steel slag, but not with the increase of bokashi of husk. The highest available P was 70.01 ppm, gained from 7.5% steel slag and 2.5% bokashi of husk. This treatment increased 60 ppm of available P compared to control.

### 3.3 Cd, Pb and Cr contents in the soils

Steel slag and bokashi of rice husk did not interact in influencing heavy metals contents in the soils. However, as an individual treatment, these ameliorants significantly influence the amount of heavy metals in the soils as displayed in Table 5. Based on the data in Table 5, it appeared that the steel slag treatments have random effect to heavy metal content. Referred to the heavy metal content in the steel slag as Cd was 0.42 mg kg⁻¹, Pb was trace, and Cr was 94.7 mg kg⁻¹ (Table 1), it was interesting that Cd content in the soils was lower than the Cd content in the steel slag. The amount of Pb in the steel slag was trace, nevertheless Pb appeared in the soils after treatment. Mean-
while, Cr content in steel slag was the highest, and it found quite high in the soils.

The steel slag influenced the heavy metals contents in different rates. The Cd and Pb contents were lowered by increasing the dosage of bokashi of husk while the Cr content remained stable. It appeared differently in Cr, where the higher steel slag applied, the higher the Cr found in the soils. The Cd and Pb content were lowered by the increasing of the dosage of bokashi of husk, meanwhile the Cr content remained stable.

Table 5 The individual effect of steel slag and bokashi of husk to Cd, Pb and Cr content in the soils

| Treatments       | Cd      | Pb      | Cr      |
|------------------|---------|---------|---------|
| Steel Slag       |         |         |         |
| 0%               | 0.13 bc | 19.50 b | 15.19 a |
| 2.5%             | 0.15 c  | 18.33 ab| 25.89 b |
| 5%               | 0.13 ab | 17.69 a | 39.87 c |
| 7.5%             | 0.11 a  | 17.58 a | 46.11 d |
| Bokashi of Husk  |         |         |         |
| 0%               | 0.15 b  | 19.68 c | 30.15 a |
| 2.5%             | 0.12 a  | 17.01 a | 32.0 a  |
| 5%               | 0.13 a  | 18.44 bc| 32.51 a |
| 7.5%             | 0.12 a  | 17.98 ab| 31.19 a |

Note: Same letters indicate no difference of the value between the treatments with Duncan Multiple Range Test 5%

Regarding to the data gained in this research, the amelioration of Andisols with steel slag and bokashi of husk showed some amounts of heavy metals in the soils. The treatments lowered the Cd and Pb content by increasing the dosage of steel slag applied, but increased the Cr content by increasing the dosage. Unfortunately, we do not have the data of heavy metals contents in soils before application with ameliorants. Therefore, some results such as notable amount of Pb in the soils while it was only trace in the steel slag could not fully discussed and has to be considered in the future research.

Figure 1 informed the difference concentration of heavy metals contents in the soils. Concentrations of Cd and Cr were the lowest and the highest, respectively. Meanwhile, concentration of Pb was in the middle rate between Cd and Cr. However, the most important aspect of these data was the whole concentrations were lower than the allowed concentration heavy metals in the soils.

The most important aspect of applied steel slag and bokashi of husk as ameliorants to the soil is the rate of this heavy metals contents after application. The permission rate of this heavy metals in the soils have to be referred to conclude whether it is safe to be applied or not. The total concentration of Cd (0.11-0.15 mg kg\(^{-1}\)) was lower than the permitted rate where 1.1 – 2.7 mg kg\(^{-1}\) (Ewers et al., 1993; McLaughlin and Singh, 1999; Alloway and Steinnes, 1999). The rate of Pb (17.01-19.68 mg kg\(^{-1}\)) was much lower than 421 mg kg\(^{-1}\) as the allowed rate of Pb (Pajak et al., 2015). The concentrations of Cr were 15.19 - 46.11 mg kg\(^{-1}\) and noted as the highest concentration in this research. However, it was still below than the permitted amount of 150-400 mg kg\(^{-1}\) according to Economou-Eliopoulos et al. (2012).
CONCLUSION

The amelioration of soils using steel slag and bokashi of husk in Andisols could decrease P-retention and increase available P. The heavy metals Cd, Pd and Cr found in the steel slag, were also detected in the soils in different concentrations. However, their total concentrations were still lower than the permitted rate of heavy metals in the soils. This finding is expected as hypothesis and can support the use of steel slag as ameliorant in the soils, since this material was previously considered as dangerous and poisonous to be used.

REFERENCES

Alloway, B. J. and Steinnes, E. 1999. Anthropogenic additions of cadmium to soils. In McLaughlin, M. J. and Singh, B.R. (Eds.). Cadmium in Soil and Plants. Springer, Netherland. p: 97 – 123.

Bielders, C.L., L.W. De Backer, B. Delvaux. 1990. Particle density of volcanic soils as measured with a gas pycnometer. Soil Science Society of American Journal. 54(3):822-826.

Blakemore, L. C., P. L. Searle, B. K. Daly. 1987. Methods for Chemical Analysis of Soils. Dept. of Scientific and Industrial Research. Lower Hutt, New Zealand.

Boniao, R. D. 2000. Amelioration of Volcanic Soils from Camiguin Island (Southern Philippines) Using Natural Amendments. Ph. D. Thesis. University Putra Malaysia.

Buchholz, D. D., J. R. Brown, D. K. Crocker, J. D. Garrett, R. G. Hanson, J. A. Lory, M. V. Nathan, P. C. Scharf, H. N. Wheaton. 2004. Soil Test Interpretations and Recommendations Handbook (Revised Edition). Division of Plant Sciences, University of Missouri, USA.

Economou-Eliopoulos, M., D. Antivachi, Ch. Vasilatos, and I. Megremi. 2012. Evaluation of the Cr (VI) and other toxic element contamination and their potential sources: The case of the Thiva basin (Greece). Geoscience Frontiers. 3(4): 523-539.

Ewers, U., I. Freier, M. Turfeld, A. Brokhaus, I. Hofstetter, W. Konig, J. Leisner-Saaber, T. Delschen. 1993. Heavy metal pollution of soil and garden products of Stolberg home gardens and lead and cadmium pollution of small farms in Stolberg. Gesundheitswesen. 55(6): 318–325.

Higa, T. 1991. Effective microorganisms: a biotechnology for mankind. In Proceedings of the First International Conference on Kyusei Nature Farming. US Department of Agriculture, Washington, DC, USA. pp. 8–14.
Ma, J., K. Nishimura, E. Takahashi. 1989. Effect of silicon on the growth of rice plant at different growth stages. Soil Science Plant Nutrition. 35(3): 347–356.

McLaughlin, M. J. and Singh, B.R. 1999. Cadmium in soils and plants, a global perspective. In McLaughlin, M. J. and Singh, B.R. (Eds.). Cadmium in Soil and Plants. Springer, Netherland. p: 1 – 9.

Navarro, C. R., M. Díaz and M. A. Villa-García. 2010. Physico-chemical characterization of steel slag. Study of its behaviour under simulated environmental conditions. Environmental Science Technology. 44(14): 5383 – 5388.

Pająk, M., M. Gasiorek, A. Cygan, T. Wanic. 2015. Concentrations of Cd, Pb and Zn in the top layer of soil and needles of scots pine (Pinus sylvestris L.); a case study of two extremely different conditions of the forest environment in Poland. Fresenius Environmental Bulletin. 24(1):71-76.

Qafoku, N. P., E. Van Ranst, A. Noble and G. Baert. 2004. Variable charge Soils, their mineralogy, chemistry and management. Advances in Agronomy. 84:159-215.

Silitonga, P. H. 2003. Geological Map of Bandung. Department of Energy and Mineral Resources.

Soil Survey Staff. 2014. Keys to soil Taxonomy 12th ed. USDA-Natural Resources Conservation Service. Washington, DC.

Van Reeuwijk, L. P. 2002. Procedure for Soil Analysis (6th edition). ISRIC, FAO. Wageningen. The Netherlands.