Identification of cobalt in paddy fields in Karawang and Bekasi Districts

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Abstract. Plants need cobalt (Co) for nitrogen fixation and encourage seedling growth. If the amount is excessive, cobalt causes a reduction in crop yield and poisoning. This study aims to monitor the toxicity levels of cobalt in paddy fields. The study was conducted in the lowland rice fields of Karawang and Bekasi regencies by taking 394 samples of topsoil. The soil samples were collected by survey method. The analysis showed that all samples contained total cobalt, ranging from 0.477 to 31.829 ppm. The data is classified into 3 classes, namely: normal, normal-toxic and toxic under the quality standards of heavy metals in the soil [7]. The classification results showed that 391 samples are categorized as the normal class, 3 samples as the normal-toxic class, and there was no sample categorized as toxic class. The results of this study can be used as a reference for stakeholders to conduct land management to avoid cobalt poisoning.

1. Introduction
Contamination of heavy metal on the water and soil will harm plant, animal and human health. It is become world’s important concern to the agricultural product. The heavy metal cumulative will toxic event at very low concentration [1]. The agricultural lands around urban area will contaminated pollution from industry activity, mining, fuel emissions, and anthropogenic activity. Pesticides and agrochemical are important to get better crop quality and improve yield, but erroneous and indiscriminate use of these organic compounds leads to the destruction of bio-control agents, pesticide residues in agro-ecosystems and environmental pollution, besides accumulating in the food chain [2].

Although it is a metal element, cobalt is necessary for life such as blue-green algae, bacteria and leguminous plants [3]. Cobalt in the soil is used by certain bacteria in plant roots to make traces of fulfilling the macronutrients necessary for healthy plant growth [4]. In animal cobalt derives from food and water, where it is used to synthesize vitamin B12. Whereas in human cobalt derives from drinking water and food, both from eating vegetables and animal products such as meat, eggs and milk. Cobalt is important for humans to form vitamin B12, which contributes to the formation of healthy blood cells and neurological health. Cobalt requirements for the body are very low with an average daily intake of about 5-8 mcg which is sufficient from daily food intake without taking supplements [5].

Besides being beneficial, it turns out that cobalt can be detrimental if the amount is excessive. Excess cobalt causes reduced yield and inhibition in assimilating production in leaves, and even inhibits the export of photo assimilates to roots and other sinks. Excess cobalt also causes oxidative stress and can lead to phytotoxicity for plants [6].
Because cobalt is very influential for plant growth, it is necessary to monitor cobalt levels in the soil so that its toxicity is known. Co critical limited on the soil are 25-50 ppm [7]. Sources of Co pollutants can come from industrial waste, household waste, mining activities, and agricultural activities [3]. Cobalt also can come from agricultural fertilizers, agrochemicals and various organic materials including sewage sludge, livestock manure, food wastes and composts [7]. This study aims to monitor the toxic levels of cobalt in rice fields. The rice field was chosen because it is a place to grow rice, which is the staple food of Indonesian society.

2. Material and methods

2.1. Study Site
The research was conducted in Bekasi and Karawang Districts, West Java in February - March 2018. The location of the sample points was determined along the river because many industries dispose of waste in the river, so that it will pollute the water used for irrigation and will also affect rice fields. The sampling method in the field used the survey method. Sampling was carried out at research sample points determined by a grid on rice field units.

2.2. Materials and Methods
One sampling point consists of 5 to 10 individual samples (sub-samples), with a distance of 25 to 50 m for each sub-sample in the field. The tool used for taking the soil sub-samples was a soil auger, which was taken from the topsoil with a depth of 20 cm. The individual samples were put in a bucket and mixed until they were homogeneous, then weighed 0.5 to 1 kg and put in a plastic bag with a size of 15 × 25 cm and wrote the sample information on the plastic, tied with wool yarn. The filling/writing of the inner label and the outer label consists of the date of collection, collection code and sample number as well as the name of the location (village and sub-district) and the type of sample. This is composite soil sample. After airing the soil sample, then milled it and sieved with a 2 mm sieve. Subsequently, soil samples were taken to the IAERI’s Integrated Laboratory for Co analysis with the wet ashing method using a mixture of concentrated acid HNO₃ (65% pa) and HClO₄ (60% pa) [8].

The results of the analysis of the heavy metal content of cobalt from the laboratory then classified according to toxicity based on [6], namely:

| Class of Toxicity | Number of Co (mg kg⁻¹) |
|-------------------|------------------------|
| Non toxic         | 0 – 25                 |
| Normal toxic      | 25 – 50                |
| Toxic             | > 50                   |

All sample points were then made a cobalt distribution map using the ArcGIS 10.3 program by considering the graduated proportional symbol according to the cobalt toxicity class. The base map comes from Indonesian Geospatial Information Agency which is downloaded at tanahair.indonesia.go.id which is the Indonesian Geospatial Portal.

3. Result and discussion
Cobalt is needed indirectly by plants, especially leguminous plants to provide N which comes from atmospheric nitrogen fixation by rhizobium bacteria. Cobalt is an essential element for rhizobium bacteria. [9]. Cobalt becomes toxic to plants when it is excessively available in the soil [7]. The impact of excess Co in the soil that is absorbed by plants is the disruption of the plant photosynthesis process [10]. The results of cobalt identification in paddy fields in Karawang and Bekasi Districts are presented in table 2.
Table 2. Descriptive Statistic of Co in Karawang and Bekasi Districts

| Parameter       | Total Sample | Mean   | Standard Deviation | Minimum | Maximum | CV (%) | Skewness | Kurtosis | VMR   |
|-----------------|--------------|--------|--------------------|---------|---------|--------|----------|----------|-------|
|                 | 394          | 13.91  | 3.28               | 0.47    | 31.83   | 23.61  | 0.51     | 3.81     | 0.77  |

The results of descriptive statistics show that the distribution of Co elements is not normally distributed where the skewness value is close to 1 and kurtosis 3. It will normally distributed if the skewness value is close to 1 and kurtosis close to 0. Based on the VMR value, the Co spatial distribution pattern spreads with a VMR value <1. The spatial distribution pattern of a clustered element in this experiment shows that it is mostly influenced by the parent material, whereas if the distribution is spread out it is influenced by anthropogenic activity [11, 12].

![Figure 1. Cobalt distribution in Karawang and Bekasi Districts](image)

The other samples of a total of 391 are included in the non-toxic class. This means that almost all research areas are safe from Co contamination because none maximum allowed concentration. Most of the area is alluvial with the main parent materials are clay and limestone. Many fertilizers contain trace amounts of heavy metals due to their origin from rocks that include high levels of trace elements [13]. It is possible that Co comes from the use of fertilizers. Research by Purbalisa [3] said high levels of Co in the top soil can be caused by anthropogenic inputs such as fertilizers and pesticides. It can be seen that more Co metal is found in the top layer (0-20 cm) while in the subsoil layer, less at the
middle layer (20-40 cm) to the lower layer (40-60 cm) the Co metal content is lower. Following is the Co content in various fertilizers used for agriculture in table 3.

**Table 3. Number of cobalt in fertilizer [13, 14]**

| Fertilizer          | Number of Co (mg kg⁻¹) |
|---------------------|-------------------------|
| Urea                | 1.0 – 1.4               |
| Ammonium Sulphate   | 7.7 – 12.0              |
| Ammonium Nitrate    | 5.4 – 11.5              |
| Superphosphate      | 8.8 – 21.0              |
| Potassium Sulphate  | 5.8 – 7.0               |
| Phosphate           | 8 – 21                  |
| Sludge              | 0.6 – 1.56              |
| Livestock Manure    | 0.3 – 24                |

The island of Java is largely characterized by a wide and rather low central depression stretching East-West, which is covered with stratovolcanoes [15]. In general, in the southern part of West Java, there are zones that are raised oblique and central depression but are not visible in several places [15]. The stratigraphy of the Karawang area consists of several formations composed of rocks such as limestone clay, limestone, claystone, conglomerate sandstone (andesite, basalt, pumice, quartz) [16]. Geological conditions in Cipurwasari Village, Tegal Waru sub-District, Karawang District, West Java, it is known that in the area there are andesite breakthrough rocks that have economic value igneous rock which can be used as raw material for industrial excavation [17].

![Geological Map of The Karawang Quadrangle, Jawa](image-url)
As seen in the geological Map of The Karawang Quadrangle most of the study area is alluvial land. It consists of sediment rock, limestone, clay stone, sand stone conglomerate, sandy limestone, and a little number of andesite. There is least parent material of Co on location. That is why Co found in small quantities.

Mineral Co is found in small quantities in nature [18] Andesite rock can be a source of Co element in the soil even though the amount is not much. Andesite rocks contain various minerals where cobalt will be associated with these minerals, for example, sulphide minerals and oxide minerals magnetite, quartz, tourmaline, calcite. As seen in 3 locations (figure 1) where the Co element is considered normal toxic, there are andesite rocks in the area and it is also close to the nickel mining industry [16, 17]. Almost all nickel mining areas in Indonesia have been explored, found low-grade nickel (Ni + Co) reserves of 1.285% amounting to 129.4 million tonnes [18].

Because the research found 3 locations have normal toxic conditions (figure, 1) maybe it necessary to reduce Co. There is some ways to reduce Co on the soil so it will be healthy soil to grow plants i.e. chemical remediation, physic remediation, bioremediation and phytoremediation. Chemical remediation and physic remediation are too expensive to do. For the last 25 years had been developed bioremediation and phytoremediation, it’s cheap and easy to do. Bioremediation using compost, activated charcoal and microbes can reduce 52.3% Co in the soil [3]. Phytoremediation development using Agrostis gigantea, Haunaniastrum robertii, Mimulus guttatus was able to reduce Co [19].

4. Conclusions

From the study we can see the toxic level of identification Co there are 391-locations non-toxic and 3-locations normal toxic of Co, it means the Co concentration in the soil is not in toxic level therefore rice plant could grow optimal and the rice grain is free from Co toxicity. The lo concentration of Co in Karawang and Bekasi District might be due to the parent materials consists of sediment rock, limestone, clay stone, sandstone conglomerate, sandy limestone, and a small amount of andesite. Bioremediation and phytoremediation can be applied to the paddy field at normal toxicity level of Co in order to reduces the Co concentration in soil.

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