Effect of pH on metal mobility in the soil

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Abstract. pH is a parameter that can be used to estimate the mobility of chemical elements in the soil and can be used to measure the level of toxicity and soil pollution. The purpose of this study is to prove how far the influence of pH on metal mobility in the soil. Method that used in this study, 35 samples each 1 kg were taken from the soil profile in Cilengsi Bogor and then dried at room temperature. From each sample 20 grams were taken for pH and Eh measurements. The result of this study that the analysis showed a significant correlation between pH and Eh with r = 0.888. Although the samples are heterogeneous or come from different soils, there is still a positive correlation between metal concentration and pH (pH-Mn = 0.12; pH-Cd = 0.0058; pH-Pb = 0.39). This means that for homogeneous samples, the correlation between pH-metals will be more significant. Eh and soil pH variations depends on the activity and decomposition of carbon by plants and microorganisms. Therefore, it can be ideally be concluded that the topsoil Eh is higher than the bottom Eh. The aerobic-anaerobic boundary is at around 300 mV.

1. Introduction
Anthropogenic metal concentrations are still causing environmental problem because they are influenced by many factors. The type and nature of soil, location, climate and methods have made it difficult to reach agreements at the international or national level [1,2]. Therefore the threshold of heavy metals contained in soil is determined based on land use (Bundes-Bodenschutz- und Altlastenverordnung [3].

pH is a parameter that can be used to estimate the mobility of chemical elements in the soil. Therefore, pH unit can be used to measure the availability of nutrients and heavy metals related to the level of toxicity and soil pollution [4,5].

The accuracy level of pH measurements by using H+ ion-selective glass electrodes can be improved by the conditions, processes and measurement times. For this purpose, as many as 20 primary samples from the field and 100 secondary samples were collected from various types of literature. Eh measurements are made to measure electrode accuracy. Most heavy metals in soil are adsorbed by Fe-Mn-Oxida. Because of that we can conclude that heavy metal concentrations are strongly correlated with pH and Eh.

Metal concentrations result from Roentgen Fluorescence Analysis and Atomic Absorption Spectrometry wet analysis can be used to control the sensitivity and accuracy of pH parameters. To limit the amount of data, Pb and Cd samples are chosen [6,7]. Samples of known concentration are used to determine the correction factor. To avoid matrix effects and to reduce error rate, wet analysis is only
done on Pb and Cd in Aqua Regia solution [8]. The objective of this study is to prove how strong the influence of pH to mobilize metals in the soil, so it can act as pollution indicator in the soil.

2. Methods
A total of 35 packets of 1 kg samples were taken from the soil profile in Cilengsi, Bogor and then dried at room temperature. From each sample 20 grams were taken for pH and Eh measurements. The remainder is homogenized to determine the concentration of the selected metal [8].

All pH measurements are carried out under the same conditions. Sample of 30 grams mixed with 75 ml of 0.1 N KCl, stirred for 30 minutes using a magnet. The pH is determined when there is no change identified after 1 minute. For pH-meter calibration, Phosphate for pH 7.02 and Phthalate for pH 4 are used.

Metal analysis was carried out by dissolving 5 grams of sample, which previously been homogenized into 40 ml of aqua regia and heated for 1 week at 80ºC, then analyzed with AAS [9].

The study was conducted from November 2018 to May 2019, with the Environmental Laboratory, Department of Environmental Health, Universitas Indonesia and the Indonesian Institute of Health as research conduction location. Samples was taken from agricultural land in Cileungsi, Bogor, West Java.

3. Results and discussion
The concentration of heavy metals as pollutants in the environment is usually expressed in total concentration. Until now only certain species have been intensively studied, especially metals that are mobile, related to waste, plants and the food chain. The metal's character to the soil and its toxicology to ecology are very much determined by the form of its compounds [8,10].

To analyze metals in the soil quantitatively and qualitatively, we can use Infrared Spectroscopy or Roengents Absorbsion Spectroscopy (XAFS). But for low concentrations the results are still unsatisfying. For this reason, the metal content extraction is done gradually according to the stability of the metal bonds in the soil. Weak acids are used for mobile metals. For highly stable species aqua regia and fluoride acid are used. The gradual extraction method cannot classify species groups, only metal mobility in the soil. This method is considered sufficient to analyze the level of soil and environmental pollutions related to geogenic and anthropogenic metal contents [4,6].

Most of the metals in the soil are in the form of adsorbed particles, colloidalally bound, in forms of inorganic and organic complex compounds or salt compounds, and oxide/hydroxide compounds [8].

The analysis showed a significant correlation between pH and Eh with r value of 0.888. Although the samples are heterogeneous or come from different soils, there is still a positive correlation between metal concentrations and pH (pH-Mn = 0.12; pH-Cd = 0.0058; pH-Pb = 0.39). This means that for homogeneous samples, the correlation between pH-metals will be far more significant.

Soil Eh and pH variations are highly depend on the activity and decomposition of carbon by plants and microorganisms. Therefore, it can ideally be concluded that the topsoil Eh is higher than the bottom Eh. The lower part of the soil is usually oxidative. The aerobic-anaerobic boundary is at around 300 mV [11,12].

The increase in pH in acidic soils happens together with the reduction. In a neutral position, protons will be depleted for the need of reduction. A decrease in pH occurs in the oxidation process. As the pH is escalating, the mobility of heavy metals is descalating, with a sequence of Cd > Zn > Ni > Cu > Pb. At pH 7, Zn and Cd ions begin to break free of their compounds, meanwhile Cd, Co, Cr as less mobile metals will begin to dissolve at pH < 5.

At pH 7 the concentration of Cd dissolved into Cd2+ ions is at 80% and at pH 5-6 Pb that dissolved into Pb2+ is at 80 to 90%.
Soils that contain a lot of air or dissolved oxygen have oxidized compounds of Fe-, Mn hydroxide, nitrate and sulfate. Thus the content of organic matter which is easily degraded is decreased which show positive redoxspot potential (up to 0.8 V). The opposite is an anaerobic reduction milieu (Eh to -35 V) containing many reduced compounds (cations of Fe2 +, Mn2 +) and organic materials that are easily destroyed such as in groundwater soil or in alluvium sites. Facultative and obligate anaerobic organisms reduce NO3- to N2O and N2, Mn4 + to Mn2 +, Fe3 + to Fe2 +, weathered organic matter to CO2, H2, low molecular alipatic acid (vinegar, buterate, milk acid etc.). This change in Eh is accompanied by a change in pH [12].

The following are the results of the analysis of the acidity (pH), Eh and total concentration of Mn, Pb and Cd.
Table 1. Levels of pH, Eh and total concentration of Mn, Pb, Cd.

| No | Mn   | Cd   | Pb   | pH   | Eh   |
|----|------|------|------|------|------|
| 1  | 523.8| 2.492857 | 1.392857 | 1.052857 | -0.63 |
| 2  | 256.6| 0.782143 | 1     | 0.952857 | 0.385 |
| 3  | 83.3 | 0.5    | 0.785714 | 0.928571 | 0.635 |
| 4  | 73.8 | 0.392857 | 1.214286 | 1.034286 | -0.4525 |
| 5  | 66.5 | 0.492857 | 0.892857 | 0.91    | 0.805 |
| 6  | 51.9 | 0.385714 | 0.857143 | 0.908571 | 0.805 |
| 7  | 60.6 | 0.567857 | 1.071429 | 0.911429 | 0.7925 |
| 8  | 78.5 | 0.332143 | 0.928571 | 0.857143 | 0.775 |
| 9  | 127.6| 0.503571 | 1.142857 | 0.944286 | 0.4625 |
| 10 | 72   | 0.532143 | 0.857143 | 0.914286 | 0.795 |
| 11 | 183.3| 1.014286 | 0.785714 | 0.945714 | 0.4575 |
| 12 | 206.6| 0.835714 | 0.857143 | 0.955714 | 0.35  |
| 13 | 89.5 | 0.371429 | 0.857143 | 0.96    | 0.3125 |
| 14 | 109.7| 0.514286 | 0.964286 | 1.081429 | -0.9175 |
| 15 | 94   | 0.45    | 0.821429 | 0.947143 | -1.0125 |
| 16 | 90.1 | 0.442857 | 0.857143 | 1.112857 | -1.2375 |
| 17 | 73.7 | 0.378571 | 1.285714 | 1.114286 | -1.2625 |
| 18 | 87.7 | 0.3    | 0.785714 | 0.955714 | -1.0975 |
| 19 | 78   | 0.325   | 0.821429 | 1.098571 | -1.0925 |
| 20 | 101.4| 0.371429 | 0.75    | 0.932857 | 0.5725 |
| 21 | 112.3| 0.296429 | 0.857143 | 0.928571 | 0.6225 |
| 22 | 84.2 | 0.3    | 0.928571 | 1.094286 | -1.0575 |
| 23 | 122.8| 0.389286 | 0.892857 | 1.11    | -1.215 |
| 24 | 125.1| 0.296429 | 1.071429 | 1.09    | -1.0075 |
| 25 | 138.5| 0.321429 | 0.892857 | 0.957143 | 0.335 |
| 26 | 122.9| 0.653571 | 1.107143 | 1.038571 | -0.49 |
| 27 | 151.5| 0.925   | 1      | 1.032857 | -0.43 |
| 28 | 124.2| 0.267857 | 1.214286 | 1.068571 | -0.7975 |
| 29 | 114.4| 0.482143 | 0.928571 | 1.061429 | -0.7225 |
| 30 | 102  | 0.317857 | 1.178571 | 1.044286 | -0.5525 |
| 31 | 132.2| 0.457143 | 0.892857 | 1.02    | -0.31 |
| 32 | 133.5| 0.571429 | 1.071429 | 1.022857 | -0.34 |
| 33 | 138.4| 0.328571 | 1.142857 | 1.018571 | -0.29 |
| 34 | 140  | 0.414286 | 1.071429 | 1.04    | -0.505 |
| 35 | 149.4| 0.435714 | 1.107143 | 1.01    | -0.1975 |
| 36 | 139.7| 0.717857 | 0.892857 | 0.924286 | 0.66  |
| 37 | 139.4| 0.471429 | 1      | 1.032857 | -0.43 |
| 38 | 115.5| 0.335714 | 0.928571 | 1.021429 | -0.3125 |
| 39 | 111.9| 0.517857 | 1.035714 | 1.042857 | -0.535 |
| 40 | 134.9| 0.357143 | 1.142857 | 1.025714 | -0.35 |
| 41 | 150.6| 0.403571 | 1      | 1.018571 | -0.2925 |
| 42 | 144  | 0.571429 | 1.071429 | 0.978571 | 0.1175 |
| 43 | 145.3| 0.432143 | 0.928571 | 1.005714 | -0.16 |
| 44 | 114.7| 0.642857 | 1.035714 | 1.005714 | -0.1525 |
| 45 | 158.5| 0.642857 | 1      | 0.994286 | 0.0425 |
| 46 | 161.6| 0.775   | 0.821429 | 1.017143 | -0.28 |
| 47 | 147.9| 0.807143 | 0.892857 | 1.041429 | -0.5175 |
Complex compounds and pH parameters are very influential on metal mobility and also on food chain concentration. Low pH means that the mobility of metals in the soil is higher which creates lower the availability of metals in the soil. The higher the pH, the lower the mobility of Cd > Zn > Ni > Cu > Pb [12]. At pH <7 Cd and Zn start to mobile at water phase or pH <5: Pb, Co, Cr, at pH [1]. At pH 7 about 80% of Cd metal is available in the form of dynamically moving Cd2+ ions, at pH 4-7 in the form of CdSO4 compounds, CdCl2 cations, CdHCO3 cations. Based on that, all three Cd species are water-soluble or mobile. At pH 5-6 around 80-90% of Pb becomes mobile in the form of Pb2+ ions and at pH > 6 in the form of PbCO3 and Pb(OH)2. The higher the concentration of natural humate and complex compounds (eg EDTA), the lower the number of heavy metal breaks away from their compounds or the lower the metal mobility in the soil so that soil toxicity would decreases. In addition to pH, oxygen is very influential on the mobility of heavy metals in the soil [13].

Water act as a transport major vector of heavy metals in the lithosphere. Solid particles in soil, aquifers, and water bodies (suspended solid, deposited sediments in lakes, rivers, seas and sediments) can become traps and become a source of heavy metals on earth’s water cycle. Geochemical phenomena that affect the presence of heavy metals are adsorption and precipitation, while dissolved complexation affects advective and dispersive transport. For this reason, pH and Eh are the main variables controlling the potential of pollutants in water and therefore the dispersion in the environment and the presence of pollutants in biota.

![Figure 2. Major element cycle and heavy metals solubility.](image)

In the soil, heavy metals are available in the form of adsorbed particles, coloidal, inorganic and organic complex compounds, salts and hydroxides/oxides [8]. PH and concentration parameters in the formation of complex compounds affect the mobility of heavy metals in the soil. At low pH, heavy metals will be released and thus the mobility will increase. The higher the concentration of natural humic substances or the formation of synthetic complex compounds, (EDTA) the fewer the compounded metal ions with complex compounds forming ligands.

Oxygen factor in the soil is highly influential on the mobility of heavy metals, especially Cr, Co, Cu, Ni, Pb, Cd, Fe and Mn. In dry soils, metal elements are available in forms of oxides compounds because most of the available oxygen is already used by plants and microorganisms.

The water/river contains dispersed particles which will settle according to their specific masses to water and form a layer of sediment at the bottom of the water. Particles in water can be non-organic (mineral) or organic (detritus) particles. The particle size is classified as follows:

| Classes          | Diameter (mm) | Classes         | Diameter (µm) |
|------------------|---------------|----------------|---------------|
| Coarse gravel    | 20-63         | Coarse silt    | 20-63         |
| Medium gravel    | 6.3-20        | Medium silt    | 6.3-20        |
| Fine gravel      | 2.0-6.3       | Fine silt      | 2.0-6.3       |
| Coarse sand      | 0.63-2.0      | Coarse clay    | 0.63-2.0      |
| Medium sand      | 0.20-0.63     | Medium clay    | 0.20-0.63     |
| Fine sand        | 0.063-0.20    | Fine clay      | <0.2          |
4. Conclusion

- The higher the granule, the larger the specific surface and organic carbon compound adsorption.
- Total heavy metal concentration in the soil has a positive correlation with pH and negative correlation with Eh.
- This correlation is highly specific for every metal compound and highly influenced by the existence of oxygen, organic compound, and soil granule fraction (especially clay mineral).

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