서울特別市 保健環境硏究論文集 第37號 (2001)
Report of S.I.H.E., 37:395~399 (2001)

EFFECT OF ARTIFICIAL ACID RAIN ON THE RELEASE OF HEAVY METAL IN SOIL

Micro Pollutant Analysis Team

Yong-suk Choi, Jong-heub Jung, Seok-won Eom, Hyun-jung Oh, and Min-young Kim

인공산성우가 토양 중금속 용출에 미치는 영향

미량물질분석팀

최용석 · 정종흡 · 엄석원 · 오현정 · 김민영

초 록

토양에는 다른 외부로부터의 오염원이 없어도 많은 중금속들이 함유되어 있다. 이들 중금속은 산성우에 의해 용출될 가능성은 적은데, 이는 토양의 완충작용이 산성우의 H^+을 중화시키고, 토양이 산성화되는 것을 방지하기 때문이다. 그러나 토양이 산성우에 계속적으로 노출되어 완충효과가 떨어지고, 토양의 pH가 낮아진 경우라면, 또 산성우의 pH가 매우 낮은 경우 중금속 용출의 가능성은 커진다.

인공산성우에 의한 토양 중금속 용출은 토양 자체의 중금속 오염 정도의 변수보다는 토양이 가지는 산도에 따라 용출 차이가 많이 났으며, 산성우의 산도에 따라서도 용출의 정도는 많은 차이를 보이고 있다. 즉 중금속 오염이 심하더라도 토양의 pH가 중성에 가깝고, 완충능이 크면, 산성우에 의한 용출은 매우 적었으며, 반대로 중금속 오염이 적은 곳이더라도 토양의 pH가 낮고 완충능이 많이 떨어진 곳에서는 중금속의 용출 정도는 매우 커졌다.

주요어 : 인공산성우, 토양, 중금속, pH, 완충능

Introduction

When acid rain touches the surface of the earth, that soil may neutralize some or all of the acidity of the acid rainwater. This ability is called buffering capacity, and without it, soil becomes more acidic. As opposed to soil with the buffering capacity, if the soil itself is already acidic, the buffering effect can be reduced to a degree where there is a chance of the release of heavy metal in soil. In this research, we carried out experiments on the release degree of heavy metal in soil by pH fluctuation of artificial acid rain, the pH and the concentration of heavy metal of the soil itself, and the relationship between them. Based on these experiments and the analysis of the pH fluctuation of the soil after adding the artificially formed acid rainwater, we could come up with an explanation on the effect that acid rain has on the release of heavy metal in soil. We selected a heavy metal-contaminated site and a rather uncontaminated site in Seoul for contrast, and formed the artificial acid rain used in the experiments, based on the pH of acid rain of the past in other areas.

Method and Material

Sampling and Pretreatment

The twenty samples were collected in Seoul from April to May in 2000. The samples were dried in a polyethylene box for a few days indoors. The dried samples were crushed in a wooden blender and a steel sieved, only the fraction 〈2 mm was analyzed.

Heavy Metal In Soil.

Each sieved sample was taken 10g, added 0.1N-HCl 50ml and then shaken for a hour in horizontal-shaker(200 times/minute, width 5cm) at 30℃ After the extract is filtered by 5B filter, analyzed in flame method by Spectra AA 880(Varian).

Extract by artificial acid rain.

Taking rather an extreme case[1,2], I formed artificial rain, the pH of which was 2.0, 2.5, 3.0, 3.5, and 5.7. Each sample was extracted by forming artificial acid rain in same method upper and analyzed in graphite method Spectra AA 880(Varian).

Result and Discussion

1. Heavy Metal In Soil - Extracted by 0.1 N-HCl

The concentration level of Cd in soils ranged from 0.025 to 0.684 mg/kg dry weight. In sample No 3, 7, comparatively high marks, the Cd values were 0.596 and 0.684mg/kg dry weight. Those of Cu and Pb were from 1.914 to 35.079 and from2.763 to 67.263 mg/kg dry weight respectively. Each Cu value was 35.1, 32.5, 20.3 and 20.5 mg/kg dry weight in sample No 3, 7, 10, 12. The concentrations of Pb also indicated comparatively high level in sample No. 8, 9, 14, 19 and each value was 31.2, 29.6, 67.3, 31.4 mg/kg dry weight. The pH value ranged from 4.4 to 8.1 and the pH values in sample No. 4, 5 and 19 were less than other samples. It says that the acidification of these samples has already been advanced much in soil. There was hardly any link between the concentration level of heavy metals and pH level itself in soil.

2. pH Fluctuation of Extract with Artificial Acid Rain

The pH fluctuation of extracts which was released by distilled water of pH 5.7 and by artificial acid rain of pH 3.5, 3.0, 2.5 and 2.0 are shown Fig. 1 The pH fluctuation of extracts which was treated with artificial acid rain of pH 2.0 and pH 2.5 was much wider than that of pH3.5 and

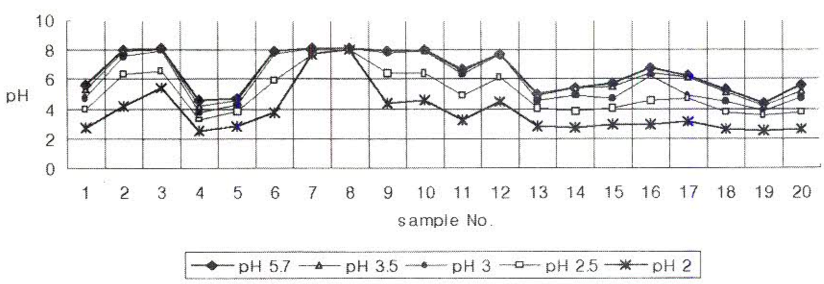

Fig. 1. pH fluctuation after extraction by artificial acid rain

3.0. The hydrogen ion originated in acid rain replaced cation in soil and it makes prevention of pH reduction. This operation is main mechanism of buffer capacity in soil. [4,5]

$Soil\text{-}M^{+} + H^{+}\ Soil\text{-}H^{+} + M^{+}$

The Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} played a major role in cation replacement in soil. When the pH drops to a level of 2.5, 2.0, or lower in acid rain, it is beyond the buffering capacity, and therefore the soil turns drastically acidic. And continuing acid rain or other factors can play a major role in accelerating the process. But there was not as much a distinct difference between pH value of extract after released distilled water and pH value of extract after released by artificial acid rain(pH 3.5, 3.0, 2.5, 2.0) in sample No. 7, 8. It shows that these samples have great buffering capacity.

Fig. 2 shows comparison of the concentration of Cd after extraction by artificial acid rain, with the concentration after extraction by 0.1 N-HCl. There was no correlation between the concentration of heavy metal extracted by 0.1N-HCl and it by artificial acid rain by simple comparison. In spite of low level of heavy metal in soil, if pH value of extract is low, the outflow of heavy metal is great. Reversibly, if pH value is high, despite high level of heavy metal in soil, the outflow of heavy metal is little.

The concentration of Cd extracted 0.1N-HCl in sample No 3, No 7 was higher than other point, but in these points the concentration of Cd extracted artificial acid rain was very low. But except the graph of Cu and Pb, the concentrations of Cu and Pb in soil comparatively were much greater than that of Cd. In terms of Cu, the concentrations in sample No. 3, 7, 10, 12 were over 20ppm, higher than other point but In No 3, 7, the concentrations of Cu extracted artificial acid rain were remarkably low. In the case of Pb, there is a similar pattern. It explains that the level of concentration in soil was not a major factor in determining how much outflow of heavy metal by artificial acid rain.

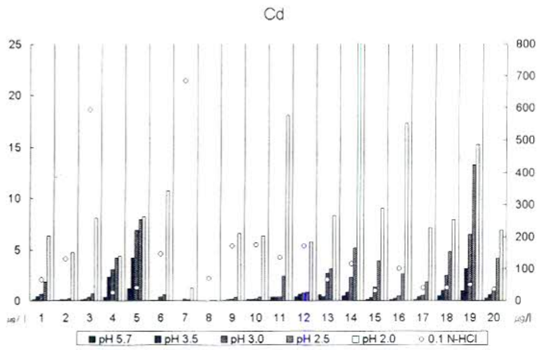

Fig. 2. The concentration of Cd after extraction by artificial acid rain and 0.1N-HCl

Fig. 3 is shown the graphs that how much effluent Cd in soil was in accordance with pH fluctuation of extract, if it treat artificial acid rain. The graph of Pb and Cu also indicated a similar trend in Fig. 3. In the pH value of extract from 2 to 3, after treatment, the concentration level of heavy metal released from soil was high relatively. But if over pH 3, the level dwindled drastically and if over 4, the level was very low.

After extraction by artificial acid rain of pH 2.0, pH values of extracts of sample No 1, 4, 5, 13, 14, 15, 16, 18, 19, 20 were less than 3.0. High level of Cd was detected in these samples. In the case of Cu and Pb values, sample 4, 14, 19 detected much high level. The concentration of Cu was over 2000ppb in sample No 14. and those of Pb were over 2000 ppb in sample No 4, 14, 19. After extraction by pH 2.5, it was a different pH value clearly comparing to extraction by pH 2.0. The pH of extract in all samples was over 3.0 and the heavy metal level was dwindled drastically. The higher pH level in artificial acid rain, the lower detected concentration of Cd abruptly.

The percentage of extraction in accordance with pH fluctuation of extract is shown Fig. 4, 5 and 6. They have tendency to be high percentage of extraction in pH value less and less. After extrac-

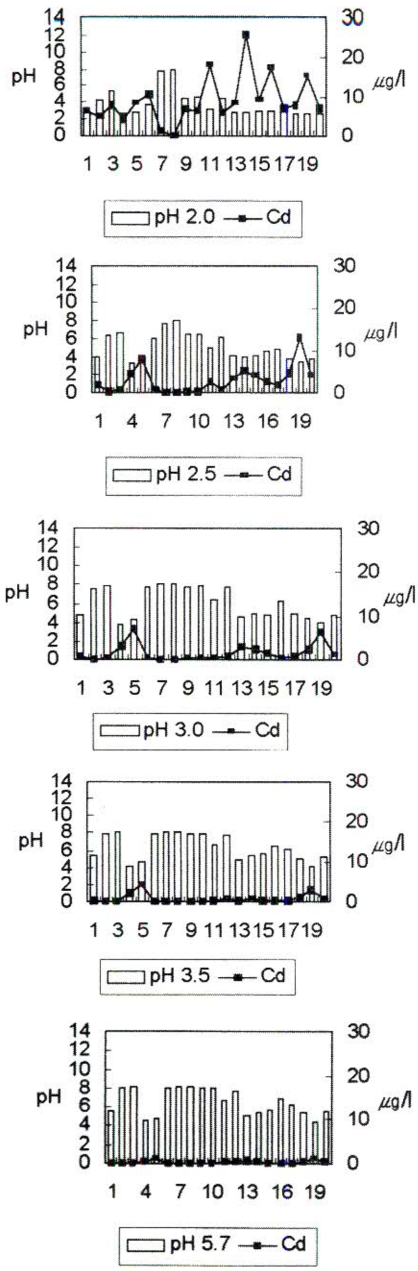

Fig. 3. Comparison of pH of extracts by artificial acid rain with concentration of Cd.

tion with artificial acid rain, the distribution graph of extract was even in case of Cd and Correlation coefficient was 0.7998. The maximum percentage of extraction also was 30% over in pH

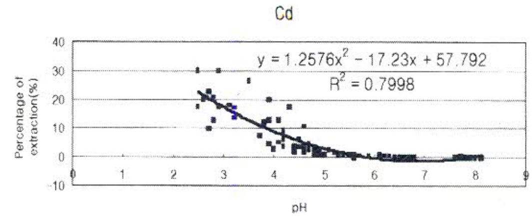

Fig. 4. Percentage of extraction in accordance with pH fluctuation - Cd

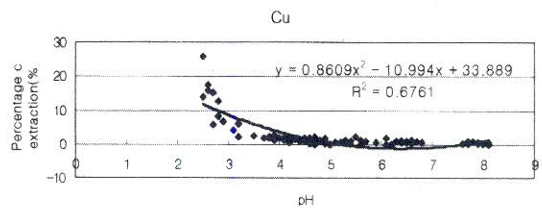

Fig. 5. Percentage of extraction in accordance with pH fluctuation - Cu

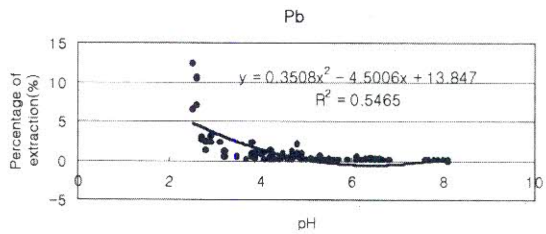

Fig. 6. Percentage of extraction in accordance with pH fluctuation - Pb

2.5. Fig. 5 indicates that Cu hardly extract in the beyond pH 3.0 of extracts and it was on increase below pH 3.0. The Pb graph says similar characteristics of distribution.

Conclusion

There is cation exchange capacity, cation absorb capacity, in soil which is worked by soil colloid. It is prevent to acidic soil, when acid rain touches the surface of the earth. The pH weighted average which the rain fell last year in Seoul was 4.8.[6) The load of this acid rain not affect easily as much as extraction of heavy metal like Cd, Pb, Cu and so forth. But once the soil becomes acidic, due to accumulating acid rain, the buffering capacity is weakened obviously, therefore possibly heavy metal release from soil.

In order to find out about the trend of heavy metal released by acid rain, We added artificially formed acid rain to soil. The result showed that if the soil itself was already acidic, the pH of the acid rain had a greater impact on it, therefore resulting in more releasing heavy metal. Also, the results showed that the pH of the soil itself and the pH of the artificial acid rain were the major factor in the level of heavy metal release from soil, rather than the concentration of the heavy metal in that soil.

References

1. Gorham E : Metroorlogical aspect of acid rain, Acid Rain, Anverview C.M.Bhumralkal Editied.Butter worth, Boston, p11-18(1984)
2. Linkens G E: Bormann F H and Johnson N M:Environment, 14(2).(1972)
3. Cohen E M: Changes in soil conditions caused by acid rain, Hazardous and industrial wastes, 31:533(1999)
4. Sullivan P J: The principle of hard and soft acids and base as applied to exchangeable cation selectivity in soils, Soil Sci., 124:117 (1997)
5. Talibudeen O: Cation exchange in soils. In d. J. Greenland and M.H.B. Hays(ed) The chemistry of soil processes, Hohn wiley and Sons. Inc., New York, pp113~177 (1982)
6. Ministry of Environment and National Institute of Environmental Research, Monthly report of air quality, Jan.~ Dec.,(2000)
7. Im Z B, Jeong T S, Kim H Y: A study on the Elution of the Soils by Acid Rain, Journal of Korean society of environmental engineers vol 18(7): 853(1996)