

## Full Length Research Paper

## Analyses of soil cadmium and copper contents on a *Domérien* soil series of Burgundy in France

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The aim of this study is to determine the availability of cadmium (Cd) in the soil of Yonne district, Burgundy, France. Soil samples were collected from surface-ploughed layer in fields across the southern part of the Yonne district, Burgundy, France. Some results analysing soil Cd and Cu contents on *Domérien* region of Burgundy has been presented. This is to know the relationship between extracting time and extracted Cd and Cu contents from the two sites' soils (Dubloc, Bierry) in the *Domérien* soil series. A total of 68-107% Cd and 20-28% Cu were extracted from the soil in 1440 min. The two soils were acidic, and around 70% of Cd contents were extracted in 20 min of extraction, while around 65% of Cu contents were extracted in 30 min of extraction. The Cd extraction was blocked at the mid-extraction time, while the Cu extraction kept on increasing up to the end of the extraction time. Cadmium extraction increased with increase in pH value in the present experiment. Copper content shows same tendency with Cd.

**Key words:** Atomic absorption spectrophotometer, cadmium availability, copper extraction, *Domérien* soil series, extracting time, soil analyses.

### INTRODUCTION

Since cadmium (Cd) occurs in zinc (Zn), lead (Pb) and copper (Cu) ores, the mining and smelting of these metals, particularly Zn and Cu, are now major sources of local environmental pollution by Cd (Piotrowski and Coleman, 1980). Cadmium content of the surface soil can vary greatly (0.14-3.51 mg Cd/kg soil) depending on soil series and sampling site (Mench et al., 1997). On

forest ecosystems, cadmium chloride concentrations in Serbian spruce [*Picea omorika* (Panc.) Purkyne] of up to 0.1 mM did not inhibit germination, while 1 mM concentration inhibited germination and the activities of catalase, superoxide dismutase and peroxidase

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(Prodanovic et al., 2012). As a result, Cd lowered the leaf contents of the photosynthetic pigments (chlorophyll a, chlorophyll b and carotenoids) in common bean (*Phaseolus vulgaris* L. cv. Nebraska) plants (Aldoobie and Beltagi, 2013), and Cd stress enhanced antioxidant enzymes, guaiacol pero-xidase, glutathione reductase, ascorbate peroxidase and polyphenol oxidase in concentration and time dependent manner in leaves of hyacinth bean (*Lablab purpureus*) (D'Souza and Devaraj, 2013). The Cd concentrations determined by EDXRF (high-sensitivity energy-dispersive X-ray fluorescence spectrometry) for ten samples of rice containing Cd at concentrations ranging from 0.05 to 2.42 mg/kg agreed with the values determined by atomic absorption spectrometry (Honma et al., 2013).

A field study was undertaken in five soil series (*Domérien*, *Carixien*, *Terres noires*, *Sols marron*, *Aubes*) from the southern part of the Yonne district, Burgundy, France (Mench et al., 1997). This area has various soil series with either low or high geochemical Cd content in the topsoil. The wheat Cd content on 5 soil series were reported as follows (Mench et al., 1997); (*Domérien* < *Carixien* < *Terres noires* < *Sols marron* < *Aubes*). After the work of Mench et al. (1997), we took the work of knowing the relations between extracting time and extracted Cd and Cu contents from the two soils in the *Domérien* soil series. The absorbance of the two mineral elements was determined by atomic absorption spectrophotometry (Arnaud, 1998; Park et al., 2008) and pH was determined. The aim of this study was to determine the availability of Cd (Etherington, 1982; Alloway, 1990) thus, some results analysing soil Cd and Cu contents on *Domérien* region of Burgundy (*Bourgogne*) in France are hereby presented.

## MATERIALS AND METHODS

Soil samples were collected on 0.3 m<sup>2</sup> area with a spade from the 0 to 0.25 m surface-ploughed layer in fields at 2 sites on *Domérien* region from the Yonne district of Burgundy, France (Mench et al., 1997). Soil samples were air-dried, 2 mm sieved and re-homogenized. And the soil samples from the *Domérien* soil series were used for the analyses of Cd and Cu contents. The names of these soils are Dubloc and Bierry.

The method for extraction was giving by Lebourg (1996) and Ghestem (1997). The time for extraction was from 5, 10, 20, 30, 60, 300, up to 1 440 min (24 h) for the two soils. And the reagent for extraction was 0.05 M EDTA (ethylene diamine tetraacetic acid) on the form of Na<sub>2</sub>H<sub>2</sub>EDTA and the soil was extracted by an agitator into a polyethylene bottle (volume around 50 ml) and the extracted solution was filtrated with a Millipore system (radius of membrane, Ø = 0.45 µm). The weight of soil and the amount of EDTA were 10 g and 30 ml, respectively. The experiment was carried out on *Laboratoire de Chimie Analytique of Institut National Agronomique Paris-Grignon* (INA P-G) in France from February 10, 1998 to January 20, 1999. The Cd and Cu contents of the extracted soil solution were determined by air-acetylene flame atomic absorption spectrophotometer (AAS) (model: VARIAN SPECTRAA 250 PLUS), and their wave lengths were 228.8 µm and 324.8 µm, respectively. A background correction mode was used for Cd analysis (Park et

al., 2008), but was not used for Cu analysis (Pinta et al., 1979).

## RESULTS AND DISCUSSION

Table 1 shows the absorbance, cadmium (Cd) content and pH values of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil, and Table 2 shows these values on Bierry soil on the *Domérien* soil series on a background correction mode.

The two soils were acidic, and the data of absorbance value was different between Tables 1 and 2. It is natural because the condition of each analysis was different. The quantity of the extracted Cd increased with the advance of extracting time (5-1440 min), and around 70% of Cd contents were extracted on 20 min of extraction. There were several factors responsible for the decision of Cd content with an atomic absorption spectrometer, for example, pH, concentration of EDTA, duration of extraction or ratio of weight/volume of solution (Ghestem, 1997).

Table 3 shows the absorbance, Cu content and pH values of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil, and Table 4 shows these values on Bierry soil on the *Domérien* soil series not on a background correction mode. Table 3 and Table 4 show the variance of the absorbance and the extractable Cu content on the 2 French soils with an atomic absorption spectrometer. The absorbance value was different from that of Kim et al. (2000), and the data between Table 3 and Table 4 was also different. Pinta et al. (1979) wrote that there are some factors which have effect on the changes of absorbance of Cu, for example, temperature, associated anion and interaction with other minerals. The quantity of the extracted Cu increased with the advance of extraction, and around 65% of Cu contents were extracted on 30 min of extraction.

Table 5 shows the comparison of soil Cd values on the *Domérien* soil series with the data of Mench et al. (1997). The total Cd, which has been obtained on humid digestion (mineralisation) with utilising HNO<sub>3</sub>, HCl and HF (Mench et al., 1997), was 0.14 (mg Cd/ kg soil) on Dubloc soil and 0.22 (mg Cd/ kg soil) on Bierry soil, respectively. And on Table 5, there was a significant difference in Cd content between those on a background correction mode and those not on a background correction mode. As written previously it is natural, because the condition of each analysis differs. There was no significant difference between total Cd (Mench et al., 1997) and Cd extractable on our present results (68-107% of total Cd).

Table 6 shows the comparison of soil Cu values on the *Domérien* soil series with the data of Mench et al. (1997). The total Cu, which has been obtained on humid digestion (mineralisation) by utilising HNO<sub>3</sub>, HCl and HF (Mench et al., 1997), was 10.4 mg Cu/ kg soil on Dubloc and 15.7 mg Cu/ kg soil on Bierry, respectively. There were big differences between total Cu (Mench et al,

**Table 1.** Absorbance, cadmium(Cd) content and pH values of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil on the Domérien soil series.

Extracting time (min) *	1**	5	10	20	30	60	300	1440
Value of natural logarithm (log e)	0.000	1.609	2.302	2.995	3.401	4.094	5.703	7.272
Absorbance (x 0.001) ***		1	2	3	3	3	4	4
		1	2	3	3	4	5	4
		1	2	3	3	4	5	4
		1	2	3	3	3	4	4
		2	1	2	3	3	5	4
		1	2	3	3	4	4	4
		1	2	3	3	4	5	4
		2	2	3	3	4	4	4
Mean absorbance		1.2	1.8	2.8	3.0	3.6	4.5	4.0
± Standard deviation (x 0.001)		± 0.4	± 0.3	± 0.3	± 0.0	± 0.5	± 0.5	± 0.0
Absorbance per 1440 min (%)		30	45	70	75	90	112	100
Cd content (mg/kg soil)	0.00	0.03	0.06	0.09	0.09	0.12	0.15	0.15
pH (measured on 21 Dec 1998)	4.64 ****	4.07	4.07	4.09	4.11	4.16	4.34	4.54

\*, 10 g soil + 30ml EDTA, and the samples were agitated and filtrated on 17–18 december 1998; \*\*, the number, 1, was used instead of 0 in order to calculate the natural logarithm value of 0; \*\*\*, Analysed with an atomic absorption spectrophotometer on a background correction mode; \*\*\*\*, the value of pH by EDTA (0.05 M).

**Table 2.** Absorbance, cadmium (Cd) content and pH values of extracted soil solution on natural logarithm value of the extracting time on Bierry soil on the Domérien soil series.

Extracting time (minutes)*	1**	5	10	20	30	60	300	1440
Value of natural logarithm (log e)	0.000	1.609	2.302	2.995	3.401	4.094	5.703	7.272
Absorbance (x 0.001) ***		4	6	8	10	10	10	14
		5	8	9	9	10	11	14
		6	8	8	9	10	12	14
		5	7	10	7	8	10	14
		6	7	10	10	10	11	11
		5	8	10	9	9	9	13
		4	5	9	8	10	10	14
		4	6	8	8	8	11	11
Mean absorbance		4.8	6.8	9.0	8.7	9.3	10.5	13.1
± Standard deviation (x 0.001)		± 0.8	± 1.1	± 0.9	± 1.0	± 0.9	± 0.9	± 1.3
Absorbance per 1440 minutes (%)		36	51	68	66	70	80	100
Cd content (mg /kg soil)	0.00	0.06	0.06	0.09	0.09	0.09	0.12	0.15
pH (03 nov 1998)		3.86	3.80	3.84	3.84	3.87	3.98	4.21
pH (06 nov 1998)		4.17	4.17	4.14	4.19	4.19	4.28	4.50

\*, 10 g soil + 30 ml EDTA, and the samples were agitated and filtrated on 2-3 november 1998 ; \*\*, the number, 1, was used instead of 0 in order to calculate the natural logarithm value of 0; \*\*\*, Analysed with an atomic absorption spectrophotometer on a background correction mode.

**Table 3.** Absorbance, copper(Cu) content and pH values of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil on the Domérien soil series.

Extracting time (min) *	1**	5	10	20	30	60	300	1440
value of natural logarithm (log e)	0.000	1.609	2.302	2.995	3.401	4.094	5.703	7.272
Absorbance (x 0.001) ***		12	12	18	20	21	26	30
		11	11	18	20	21	26	30
		12	11	17	20	21	26	31
		12	12	17	20	21	26	30
		11	12	18	20	21	26	30
		11	11	18	21	21	26	30
		11	12	17	20	20	26	30
		11	12	17	20	21	26	30
Mean absorbance		11.3	11.6	17.5	<u>20.1</u>	20.8	26.0	30.1
± Standard deviation (x 0.001)		± 0.5	± 0.5	± 0.5	<u>± 0.3</u>	± 0.3	± 0.0	± 0.3
Absorbance per 1440 minutes (%)		37	38	58	<u>66</u>	69	86	100
Cu content (mg/kg soil)	0.0	0.9	0.9	1.5	1.5	1.8	2.1	2.4
pH (measured on 21 dec 1998)	4.64 ****	4.07	4.07	4.09	4.11	4.16	4.34	4.54

\*, 10 g soil+30ml EDTA, and the samples were agitated and filtrated on 17–18 December 1998; \*\*, the number, 1, was used instead of 0 in order to calculate the natural logarithm value of 0; \*\*\*, Analysed with an atomic absorption spectrophotometer not on a background correction mode; \*\*\*\*, the value of pH by EDTA (0.05 M).

**Table 4.** Absorbance, copper(Cu) content and pH values of extracted soil solution on natural logarithm value of the extracting time on Bierry soil on the Domérien soil series.

Extracting time (min) *	1**	5	10	20	30	60	300	1440
Value of natural logarithm (log e)	0.000	1.609	2.302	2.995	3.401	4.094	5.703	7.272
Absorbance (x 0.001) ***		43	92	106	108	115	141	166
		42	92	106	110	116	143	163
		42	94	106	109	117	144	167
		42	89	104	108	114	137	160
		42	90	104	108	118	141	170
		41	91	106	108	115	144	174
		42	92	106	108	116	142	176
		42	92	107	108	117	141	173
Mean absorbance		42.0	91.5	105.6	108.3	116.0	141.6	168.6
± Standard deviation (x 0.001)		± 0.5	± 1.5	± 1.0	± 0.7	± 1.3	± 2.2	± 5.6
Absorbance per 1440 minutes (%)		24	54	62	64	68	83	100
Cu content (mg /kg soil)	0.0	1.2	2.4	3.0	3.0	3.3	3.9	4.5
pH (03 nov 1998)		3.86	3.80	3.84	3.84	3.87	3.98	4.21
pH (06 nov 1998)		4.17	4.17	4.14	4.19	4.19	4.28	4.50

\*, 10 g soil +30 ml EDTA, and the samples were agitated and filtrated on 2–3 November 1998; \*\*, the number, 1, was used instead of 0 in order to calculate the natural logarithm value of 0; \*\*\*, Analysed with an atomic absorption spectrophotometer not on a background correction mode.

1997) and those of our present results (20-28% of total Cu). But the range of this decrease was not as large as

that of Cd contents as shown in Table 5. Ghestem (1997) utilized an acidic pH and a neutral pH conditions, and the

**Table 5.** Comparison of soil cadmium(Cd) values on the Domérien soil series with the data of Mench et al. (1997) (mg Cd/ kg soil).

Soil series	Place	Cd extractable 2)*	Cd extractable 3)*	Cd extractable 4)**	Cd 3)/total Cd (%)	Cd 4)/ total Cd (%)
Domérien	Dubloc	0.21	0.12	0.15	85	107
"	Bierry	0.24	0.15	0.15	68	68

1) The total Cd, which has been obtained on humid digestion (mineralisation) with utilising HNO<sub>3</sub>, HCl and HF (Mench et al, 1997), was 0.14 (mg Cd/ kg soil) on Dubloc soil and 0.22 (mg Cd/ kg soil) on Bierry soil, respectively.

2) 10 g soil and 30 ml EDTA of 0.05 mol, it was extracted and filtrated on 19-20 october 1998. The value was obtained with an atomic absorption spectrophotometer not on a background correction mode, and the duration of extraction, it took 14 minutes and 34 minutes for Dubloc and Bierry soil, respectively;

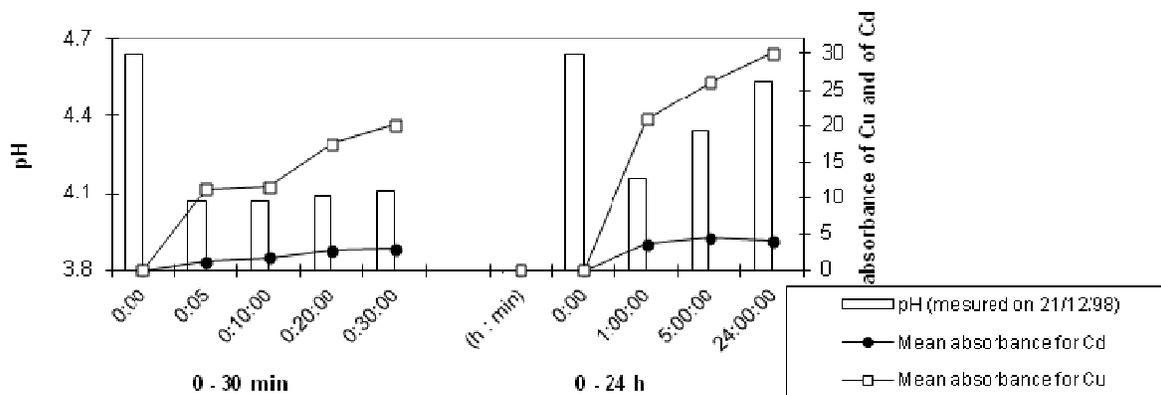
3) The same method with that of 2), but the sampels were measured with an atomic absorption spectrophotometer on a background correction mode;

4) Extraction of Dubloc soil shown on Table 1 (17–18 december 1998) and of Bierry soil on Table 2 (2-3 november 1998) during 1440 min, and it was analysed on a background correction mode; \*, One sample ; \*\*, One sample with 8 repeats.

**Table 6.** Comparison of soil copper(Cu) values on the Domérien soil series with the data of Mench et al.(1997) (mg Cu/ kg soil).

Soil series	Place	Cu extractable 2) *	Cu extractable 3) **	Cu 2)/total Cu(%)	Cu 3)/total Cu(%)
Domérien	Dubloc	2.1	2.4	20	23
"	Bierry	4.2	4.5	26	28

1) The total Cu, which has been obtained on humid digestion (mineralisation) with utilising HNO<sub>3</sub>, HCl and HF (Mench et al, 1997), was 10.4 (mg Cu/ kg soil) on Dubloc and 15.7 (mg Cu/ kg soil) on Bierry, respectively. 2) 10 g soil and 30 ml EDTA of 0.05 mol, it was extracted and filtrated on the period of 19-20 october 1998. The value was obtained with an atomic absorption spectrophotometer without background correction, and the duration of extraction, it took 14 and 34 min for Dubloc and Bierry soil, respectively, 3) Extraction of Dubloc soil shown on Table 3 (17–18 december 1998) and of Bierry soil on Table 4 (2-3 november 1998) during 1440 min, and it was analysed on not background correction mode; \*, One sample; \*\*, One sample with 8 repeats.

**Figure 1.** Absorbances of Cd and of Cu on Dubloc (Domerien) soil with an atomic absorption spectrophotometer.

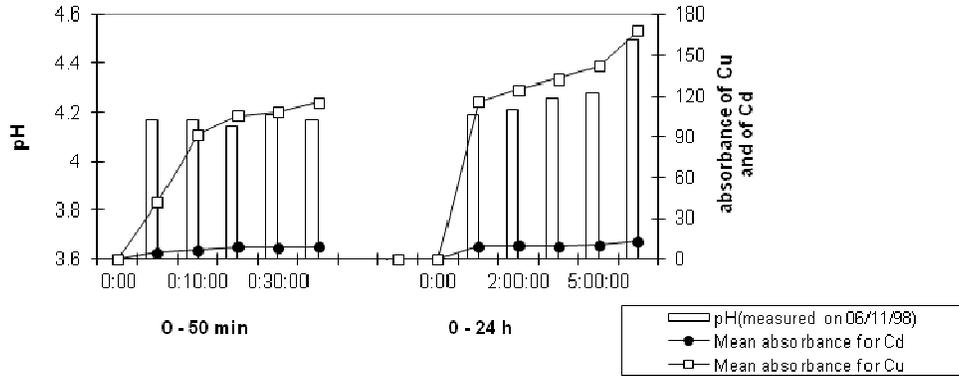
Cd content in the edible parts of vegetable species decreased with the increase of soil pH (Togami et al., 2011). In our work, Figure 3 shows the Cd content and pH value of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil on the Domérien soil series. These data were taken from Table 1. The Cd contents on 20 min (4th) and 30 min extraction (5th) were stable. And Figure 4 shows the Cu content and pH value of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil on the Domérien soil series.

These data were taken from Table 3. Here, the Cu con-

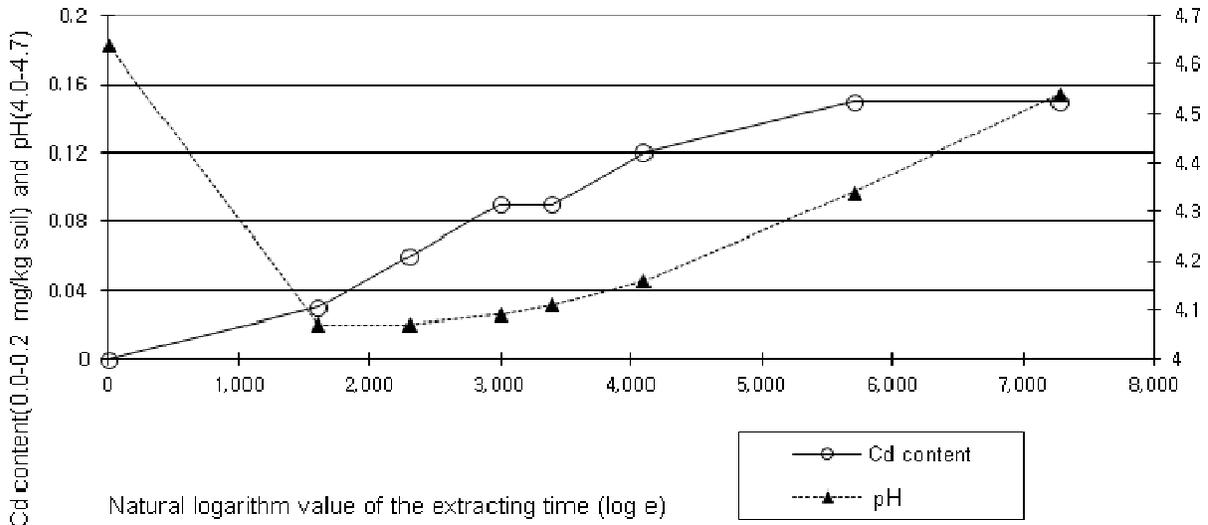
tents on 5 min (2nd) and 10 min (3rd), 20 min (4th) and 30 min extraction (5th) were stable. Figure 1 shows the absorbances of Cd and of Cu on Dubloc (Domerien) soil with an atomic absorption spectrophotometer, and Figure 2 shows the absorbances of Cd and of Cu on Bierry (Domerien) soil with an atomic absorption spectrophotometer.

## Conclusion

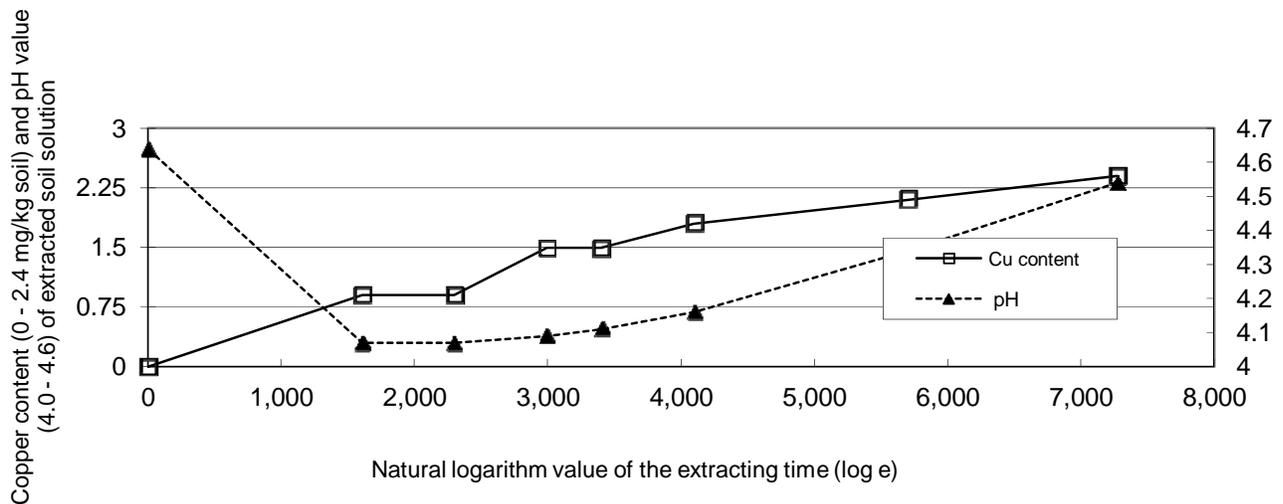
The Cd content increased on higher pH range when



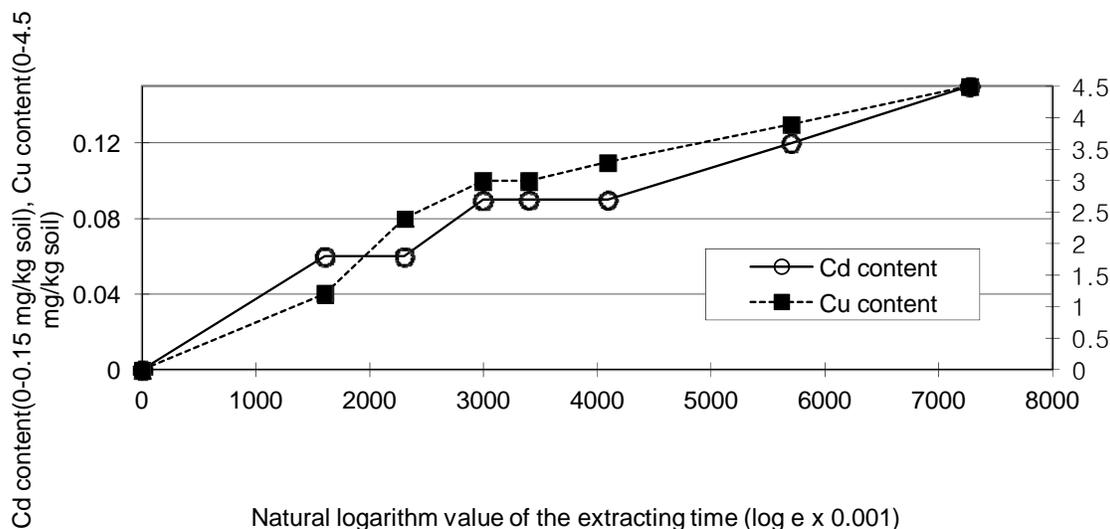
**Figure 2.** Absorbances of Cd and of Cu on Bierry (Domerien) soil with an atomic absorption spectrophotometer.



**Figure 3.** Cadmium(Cd) content and pH value of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil on the Domérien soil series (These data were taken from Table 1).



**Figure 4.** Copper(Cu) content and pH value of extracted soil solution on natural logarithm value of the extracting time on Dubloc soil on the Domérien soil series (These data were taken from Table 3)



**Figure 5.** Cadmium(Cd) and copper(Cu) contents of extracted soil solution on natural logarithm value of the extracting time on Bierry soil on the Domerien soil series (These data were taken from Table 2 and Table 4).

varied in the present experiment. The Cu content showed same tendency with Cd, while the (Cu extractable/Cu total) ratio was significantly lower value of 20-28% than that value of the Cd ratio (Cd extractable/Cd total) of 68-107%. The Cd content was blocked in the middle of extracting time, while the Cu content kept continuing increasing upto the end of the extracting time. Therefore, the soil Cd could have a stronger effect on grain Cd content than those of Cu content.

### Conflict of Interests

The author(s) have not declared any conflict of interests.

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continuous reading of the manuscript.

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