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EDTA Extractable Arsenic in Relation to Available Forms in Soil

ABSTRAK

Sepuluh sampel tanah dari kebun koko diekstrak dengan 10 mM larutan EDTA pada nisbah berat tanah/larutan 1/25. Arsenik dalam ekstrak ditentukan dengan kaedah pengeluaran hidrida – spektrometri pancaran plasma gandingan aruhan. Arsenik yang diekstrak oleh EDTA menunjukkan korelasi positif yang penting dengan Al-As, Fe-As dan arsenik yang diekstrak dengan kaedah-kaedah Mehlich I dan III, Bray PI dan Olsen.

ABSTRACT

Ten soil smaples from cocoa estates were extracted with 10 mM EDTA solution at a soil/solution weight ratio of 1/25. Arsenic in the extract was determined by hydride generation inductively coupled plasma atomic emission spectrometry. EDTA extractable arsenic showed significant positive correlation with Al-As, Fe-As, and arsenic extracted by the methods of Mehlich I and III, Bray P1 and Olsen.

INTRODUCTION

Methods to assess plant available phosphours have long been established (Wolf and Baker, 1985; Dancer, 1984; Sharplay *et al.*, 1984; Robertson, 1961). As there is a close chemical relationship between phosphates and arsenates, similar methods have been used to measure available arsenic in soils. These methods include Bray PI (Jacobs and Keeney, 1970), mixed-acid or Mehlich I (Woolsen, 1972; Woosen *et al*, 1971), bicarbonate or Olsen (Woolsen *et al.*, 1971; Merry, Tiller and Alston, 1986) and summation of inorganic arsenate fractions separated by the modified method of Chang and Jackson (Woolsen *et al.*, 1971). Most of these methods involve rather strong acids, and are not normally used to assess other available elements in soils.

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent for many metals. It has been widely used in the assessement of many inorganic elements such as copper, zinc, manganese, cadmium, and lead in soil (Osiname *et al.*, 1973; Khan and Frankland, 1983; Ure and Barrow, 1970). EDTA is also found to be an useful extractant for estimating plant-available molybdenum and selenimum (Williams and Thorton, 1973). Inorganic phosphates and arsenates occur mainly as relatively insoluble compounds of aluminium, iron and calcium in soil. If EDTA can form complexes with these metals, thus releasing phosphorus and arsenic to be measured as plant available fractions, it would be possible to have one extractant for the determination of all the available elements of interest. The feasibility of assessing available phosphorus by EDTA extraction has been reported (Sahrawat 1977; Nnadi *et al.*, 1973, Alexander and Robertson, 1972). However, there has been no such study on arsenic. The present study investigates the feasibility of using EDTA as an extractant for arsenic and compares the results with other extraction techniques.

MATERIALS AND METHODS

Soil

Ten surface samples (0–15 cm) which are composits of twenty samples collected from various cocoa estates in Peninsular Malaysia were selected. They belonged to different soil series, and had a wide range of pH, organic matter, total arsenic content, inorganic arsenic forms and extractable arsenic according to Mehlich I, Mehlich III. Bray PI and Olsen method (Table 1). The soil samples were air-dried and ground to pass a 2 mm sieve before use. Three of the ten soils, namely Rengam A,

TABLE 1
Parameters of soil samples

Soil Series	pH in water (%)	Organic matter ($\mu g\ g^{-1}$)	Total As ($\mu g\ g^{-1}$)	Al-As ($\mu g\ g^{-1}$)	Fe-As ($\mu g\ g^{-1}$)	Ca-As ($\mu g\ g^{-1}$)	Mehlich I-As ($\mu g\ g^{-1}$)	Mehlich III-As ($\mu g\ g^{-1}$)	Bray PI-As ($\mu g\ g^{-1}$)	Olsen -As ($\mu g\ g^{-1}$)	EDTA -As ($\mu g\ g^{-1}$)
Rengam A	5.30	18	21.75	2.00	8.94	3.23	1.34	1.28	1.90	2.11	0.42
Rengam B	5.78	9	16.35	1.39	6.39	2.82	1.26	0.91	1.56	1.78	0.73
Bernam	4.57	23	32.45	3.64	10.49	8.03	3.41	2.95	4.19	3.46	3.88
Tongkang	4.55	28	35.20	3.06	10.17	4.54	3.42	2.35	3.83	2.88	3.74
Jawa	4.57	24	23.75	2.96	5.47	10.58	2.75	1.39	3.43	1.51	1.84
Selangor	5.22	25	35.15	1.44	11.36	14.03	1.88	1.32	1.04	2.50	1.70
Briah	4.90	25	63.15	9.19	17.42	7.47	9.16	6.91	10.49	7.71	8.76
Munchong	5.02	10	42.65	1.01	14.33	3.46	1.29	0.75	0.84	1.82	0.40
Durian	4.90	11	34.35	0.78	9.58	5.08	1.08	0.60	0.63	1.54	0.28
Malacca	5.90	9	78.85	5.18	22.11	11.50	4.24	3.53	5.79	6.13	4.40

Briah and Munchong were chosen for detailed study of EDTA extraction.

EDTA Extraction

A stock solution of 100 mM EDTA was prepared from the disodium salt. Other concentrations of EDTA were prepared by sequential dilutions of the stock solution with deionised distilled water. As there was no information regarding EDTA as an extractant for arsenic in soils, the effects of EDTA concentration, soil/solution ratio and time of shaking on amount of arsenic extracted were studied.

Available Inorganic and Total Arsenic

Available arsenic was determined using the following extraction methods:

Mehlich I (Nelson, Mehlich and Sinters, 1953), Mehlich III, a modified version of the former method (Mehlich, 1984), Bray PI (Bray and Kurtz, 1945) and Olsen (Olsen *et al.,* 1954).

Inorganic arsenic forms were determined by the modified method of Chang and Jackson (Peterson and Corey, 1966).

Total arsenic in soil was determined after the soil sample was digested with concentrated nitric and sulphuric acids. (Van der Veen *et al.,* 1985).

Arsenic Determination

The soil extracts were filtered through No. 42 Whatman paper. The acidity of the extracts was adjusted with concentrated HCl, and arsenic was determined by hydride generation-inductively coupled plasma atomic emission spectrometry (Lee and Low, 1987).

RESULTS AND DISCUSSION

EDTA Extraction

The concentration of EDTA must be strong enough to react with all releasable di and trivalent cations, resulting in detectable amounts of arsenic in the extracts. The amount or arsenic detected did not vary greatly between concentrations of 5 and 50 mM (Table 2) However, there was an appreciable increase at 100 mM. As there tends to be recrystallization of EDTA salt at concentrations above 50 mM on standing, 10 mM EDTA was selected for subsequent studies.

As the soil/solution ratio because wider, more arsenic was released from the soil (Table 3). The increase of arsenic released from the ratio of 1/25 to 1/50 is less than 6%, and the accuracy of arsenic measurement decreased with greater soil/solution ratio. Hence the ratio of 1/25 was selected as optimum.

More arsenic was released as the time of shaking was increased from 5 minutes to 4 hours (Table 4). However, equilibrium appeared to be attained at about 2 hours. Hence a shaking time of 2 hours was selected as the extraction time.

TABLE 2
Effect of EDTA concentration on the amount of As extracted at a soil/solution ratio of 1/25 for 2 hours

EDTA Concentration (mM)	As extracted ($\mu g\ g^{-1}$)		
	Renggam A	Briah	Munchong
100	0.95	14.10	0.89
50	0.58	8.96	0.41
10	0.42	8.76	0.40
5	0.42	7.17	0.40
1	0.35	4.29	0.34

TABLE 3
Effect of soil/solution ratio on the amounts of As extracted with 10 mM EDTA for 2 hours As extrated ($\mu g\ g^{-1}$)

Soil/solution	Rengam A	Briah	Munchong
1/5	0.25	5.40	0.17
1/10	0.30	6.17	0.26
1/25	0.42	8.96	0.40
1/50	0.45	9.36	0.42

TABLE 4
Effect of time of extraction on the amount of As extracted at a soil/solution ratio of 1/25 with 10 mM EDTA

Time of Extraction (min)	As extracted ($\mu g\ g^{-1}$)		
	Renggam A	Briah	Munchong
5	0.26	3.67	0.22
15	0.31	5.68	0.24
30	0.33	5.89	0.28
60	0.42	6.69	0.36
120	0.42	8.76	0.40
240	0.44	9.97	0.48

The pH of 10 mM EDTA was 4.5. After extraction, the pH of EDTA extracts ranged from 4.0 to 4.6, depending on the pH of the soils. As the stability constants of aluminium and iron with EDTA tend to approach maximum values at pH 5 and that of Ca at pH 11, EDTA chelates mainly aluminium and iron in an acidic to neutral medium and calcium in an alkaline medium (Welcher, 1958). Thus it would be expected that for all the soils, EDTA extracted arsenic was mainly derived from aluminium and iron compounds. This is shown in the strong correlation between EDTA extracted arsenic and the arsenic bound to aluminium (Al-As) and iron (Fe-As). Correlation between EDTA-As and Ca-As was not signifacant (Table 5).

TABLE 5
Correlation between EDTA extractable As and other soil parameters

Parameters	Correlation coefficient
Total As	0.66 *
Al-As	0.97 ***
Fe-As	0.58 ±
Al-As + Fe-As	0.76 **
Ca-As	0.31
Mehlich I-As	0.98 ***
Mehlich III-As	0.98 ***
Bray PI-As	0.97 ***
Olsen-As	0.92 ***
Organic matter	0.46
Total Inorganic As	0.74 *

± P = 0.1
* P = 0.05
** P = 0.01
*** P = 0.001

EDTA Extractable Arsenic and Other Soil Parameters

EDTA extractable arsenic from ten soils using 10 mM EDTA at a soil/solution ratio of 1/25 and shaking time of two hours are shown in Table 1. The EDTA extractable arsenic showed positive correlation with inorganic forms of arsenic in soil, but its correlation with organic matter was not significant (Table 5). This indicates that EDTA extactable arsenic can only be related to arsenic present as inorganic compounds in soil. EDTA-As showed highly significant correlation with extractable arsenic determined by the methods of Mehlich I, Mehlich III, Bray PI and Olsen. As these techniques have been shown to be positively correlated to plant-available arsenic (Robertson, 1961; Woolsen *et al.*, 1971; Jacobs and Keeney, 1970) EDTA appears to be a good

extractant for the determination of plant available arsenic.

CONCLUSION

EDTA appears to be a good extractant for the determination of available arsenic in soils. The amount of arsenic extracted by EDTA is comparable to and correlates strongly with that extracted by other techniques.

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