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EFFECT OF DIFFERENT FORMS AND SOURCES OF ARSENIC ON CROP YIELD AND ARSENIC CONCENTRATION

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Abstract. Two greenhouse experiments were conducted to investigate the effects of different sources of As application on the yield of ryegrass (*Lolium perenne L.*) and barley (*Hordeum vulgare L.*) and the arsenic concentration in crop tissue. The soils used were a sand and a loam soil. In the first experiment (3 yr), As was applied either as sodium arsenite or as disodium hydrogen arsenate at the rate of 0, 2, 10, 50, and 250 mg As kg^{-1} soil in year 1. In years 2 and 3, only the residual effect of As applied in year 1 was investigated. In the second experiment (5 yr), a NPK(16–7–12) fertilizer containing 10, 100 and 3000 mg As kg^{-1} as sodium arsenite was applied at rates of 750 and 600 mg kg^{-1} to ryegrass and barley, respectively, with lime and without lime. Arsenite had more inhibitory effect on crop yield than arsenate. Although the residual effect persisted up to year 3, it was found to be dependent on As application rate, soil type, and crop species. Only minor differences in As concentration in crops between arsenite and arsenate sources were observed. The yield reduction and the increase of As concentration in crops was highly related to As application rates. The As rates of 50 and 250 mg As kg^{-1} resulted in significant yield reduction and marked increase of As concentration in both crops and these rates could be considered as critical for both crops. The application of As containing fertilizer had little or no effect on crop yield. The As concentration in both crops was little affected by the fertilizer containing up to 100 mg As kg^{-1} but the concentration increased several folds when the fertilizer containing 3000 mg As kg^{-1} was applied. The application of additional P to the treatment containing 3000 mg As kg^{-1} fertilizer only slightly increased crop yields but it increased As concentration in ryegrass markedly. The repeated application of As containing fertilizer up to a period of 5 yr, even at 3000 mg As kg^{-1} level, generally did not affect either the yields or the As concentration in both crops although a slight increase of As concentration in barley grain over the years was observed. In both experiments, the yield reduction and the increase in As concentration in crop tissue were lower in the loam soil than in the sand and barley straw cointained much higher As than barley grains, indicating that greater proportion of the As taken up by this crop was retained in the vegetative organs.

1. Introduction

Agricultural inputs such as fertilizers, pesticides, and desiccants are the major sources of As in soils. A number of cases of As contaminant of agricultural soils have been reported (Woolson *et al.*, 1971a; Hess and Blanchar, 1971; Davis *et al.*, 1978; Kitagishi and Yamane, 1981). The levels of As in N and K fertilizers as well as lime are generally considered to be small (O'Neill, 1990). However, some rock phosphate sources have been reported to contain high concentrations of As (Gunnasson, 1983) and the fertilizer produced from such rock phosphate may contain high concentration of As. Therefore possible As accumulation in

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soils due to repeated appliation of As containing fertilizers may raise the levels of As concentration in crops grown on such soils. Phytotoxicity caused by As is dependent upon the sensitivity of a crop (Deuel and Swoboda, 1972a; Woolson, 1973) and, therefore, the crop tolerance to As may differ markedly among species (Jacobs *et al.*, 1970a). Gain and edible seeds accumulate less As than other parts of the plants (Macphee *et al.*, 1960; Jacobs *et al.*, 1970b).

Arsenic exists in several oxidation states but arsenite and arsenate are the main forms of As in soil solution (Bohn, 1976). Arsenate dominates under aerobic conditions (Peterson *et al.*, 1981; O'Neill, 1990), whereas arsenite dominates under reducing conditions (Deuel and Swoboda, 1972b; O'Neill, 1990). Elemental arsenic and arsine can also exist in strongly reducing environments (Walsh and Keeney, 1975). Woolson (1973) stated that regardless of the form in which the arsenical is applied, it is eventually oxidised and metabolished to arsenate. Arsenite is considered to be more soluble and mobile (Gulens *et al.*, 1979), and more toxic to plants than arsenate (Sachs and Michael, 1971; Porter and Peterson, 1977). Arsenate, being similar to phosphorus, is easily fixed by soil components, such as Fe and Al minerals (Jacobs *et al.*, 1970a; Akins and Lewis, 1976). O'Neill (1990) found that the sorption of arsenate was greater for both Fe and Al hydroxides than that of arsenite.

The effect of As added to soils may be influenced by a number of factors, such as fertilizer application rate, soil texture, soil pH, and crop species grown. Woolson (1972) indicated that fertilizers, especially phosphate fertilizers, significantly affected plant growth, available As, and As concentration in corn plants. Due to similarity in behaviour of arsenate and phosphate ions, antagonistic or synergistic effects of P on As uptake by plants have been reported. The reduction in As uptake by a number of crops with increased levels of phosphorus application was reported by many investigators (Hurd-Karrer, 1939; Benson, 1953; Woolson *et al.*, 1973). In other studies, P has been shown to increase the available soil As and As concentration in plants at a comparable soil As level (Woolson, 1972, 1973). In such cases, P can replace As from adsorption sites and thereby can result in higher available As levels in the soil. Apart from P, N fertilizers, lime, and sulphate have also been observed to affect the As availability to plants. These nutrients or amendments were found to either depress or alleviate the As toxicity (Woolson, 1972; Peterson *et al.*, 1981; Merry *et al.*, 1986a.).

The high rates of As application were closely related to the reduction of crop yield (Woolson *et al.*, 1971b) and the increase in As concentration in plants (Thoresby and Thornton, 1979). Sadiq (1986) found that As concentration in corn plants was well correlated to the water extractable As but not to the total As in the soils. The As uptake by plants was higher and its toxicity more severe in the light textured soils than in the heavy textured soils (Deuel and Swoboda, 1972a; Woolson, 1973; Merry and Tiller, 1986). The role of soil pH on As uptake by plants is not clearly understood. Merry *et al.* (1986b) found that As uptake was less sensitive to the changes of soil pH than to As concentration. In contrast, Everett (1962)

TABLE I

Selected chemical properties of the soils used in this study

Soil	pH	P-Al	K-Al	Mg-Al	As	Cu	Fe	Al	Clay	Org. C
	(H_2O)	mg kg^{-1}							%	
Sand	5.6	2.1	26	0.3	<0.3	0.2	0.60	0.09	3	0.4
Loam	4.9	9.5	9.2	4.7	<0.3	1.8	1.32	0.23	19	3.1

reported that the increasing pH levels of grassland soils decreased the uptake of As by plants.

This work was undertaken to study: (1) the effect of arsenite and arsenate forms of As on crop yield and the As uptake by ryegrass (*Lolium perenne L.* and barley *Hordeum vulgare L.*, grown in two soils of different texture; (2) the residual effect of the As forms initially applied; (3) As uptake by these crops from a NPK fertilizer containing varying levels of As as influenced by liming, soils texture, and P application.

2. Materials and Methods

Two experiments in the greenhouse were conducted at the Agricultural University of Norway, Aas, Norway. The first experiment was carried out for 3 yr to investigate the effect of arsenite and arsenate forms of As on crop yield and As concentration in crop tissue. The second experiment was conducted for 5 yr to study the effect of As contained in a NPK fertilizer on crop yield and As concentration in crop tissue.

2.1. Soils and Plants Used

The soils used in both experiments were a sand (Typic Udipsamment) and a loam soil (Humaquept), collected from Aas, Norway (59°40′ N and 10°43′ E). Both soils were dried, passed through a 2 mm sieve, and thoroughly hand-mixed prior to use. The chemical properties of the soils are shown in Table I. Ryegrass (*Lolium perenne* L.) and barley (*Hordeum vulgare* L.) were grown as test crops in the two experiments.

2.2. Experiment 1

Arsenic was added either as sodium arsenite ($NaAsO_2$) or disodium hydrogen arsenate (Na_2HAsO_4) at the rates of 0, 2, 10, 50, and 250 mg As kg^{-1} soil. The higher rates of As at 50 and 250 mg kg^{-1} were applied in this experiment in an attempt to investigate the potential toxicity of As to plants. There were a total of 9 treatments. Nitrogen, P and K were applied in the forms of $Ca(NO_3)_2$, $Ca(H_2PO_4)_2$ and K_2SO_4 as basal fertilizers to all pots at the rates of 120, 30, and 120 mg kg^{-1}

soil, respectively. An additional dose of P at the rate of 15 mg kg^{-1} was adde to the sand. In order to avoid eventual deficiencies in the sand, a micronutrie mixture containing Mg, Mn, Cu, Mo, and B was applied at the rates of 40, 1 7.3, 0.6, and 0.3 mg kg^{-1}, respectively. Zinc deficiency is usually not a proble in these soils and hence zinc was not part of the fertilization scheme. During th growth period of ryegrass, N at the rate of 60 mg kg^{-1} was applied after eac cutting but K at the same rate was added only after the third and fourth cuttings fc supplementary fertilisation. All the fertilizers and micronutrients were thoroughl mixed throughout the 6.67 L of soil (about 8 kg), which was later on filled into 7-l plastic pots.

Arsenic was added only in year 1 and the residual effects of As applied in year were investigated in years 2 and 3. After the final harvest, the soil filled-pots were kept in the greenhouse and used again in year 2. Before planting in year 2, the soi from each pot was removed, mixed with the fertilizers and micronutrients at the same rates as in year 1, and returned to the same pot. Supplemental N was appliec in the same way as in year 1 but additional K at the rate of 60 mg kg^{-1} was only applied once to the ryegrass. In year 2, the composite plant samples of ryegrass for As determination were taken in the same way as in year 1, but barley plant samples were separeted into grain and straw. The procedure described for year 2 was repeated in year 3.

2.3. Experiment 2

A NPK fertilizer (16–7–12), prepared by the Norsk Hydro, which contained 10, 100, and 3000 mg As kg^{-1} of fertilizer as sodium arsenite was used as arsenic source in this experiment. Sodium arsenite was added to the fertilizer during manufacturing process and thus As was an integral part of the fertilizer used. The high level As of 3000 mg kg^{-1} in fertilizer was employed to see if it causes any adverse effects on crop although such high concentration of As in fertilizer is not common. However, some rock phosphates from Sweden have been found to contain as much as 235 mg As kg^{-1} (Gunnarsson, 1983). Arsenic applied through NPK fertilizer at this rate was equivalent to 1.9 mg kg^{-1} soil. The initial dose of fertilizer was 600 and 750 mg kg^{-1} soil to barley and ryegrass, respectively. In ryegrass, an additional dose of NPK fertilizer at the rate of 350 mg kg^{-1} was applied after each cutting. In order to investigate the effects of P on As uptake by plants, an additional dose of P as $Ca(H_2PO_4)_2$ at the rate of 51 mg kg^{-1} was added to the treatment containing 3000 mg As kg^{-1} fertilizer in the sand. This resulted in four treatments in the sand versus three in the loam soil. The additional dose of P was roughly equal to the intial dose of P added.

The experiment was carried out with or without lime. In the limed pots, soil pH was adjusted to about 6.5 with $CaCO_3$. The rates of liming in year 1 were equivalent to 1800 and 3000 mg kg^{-1} in the sand and the loam soils, respectively. Additional doses were applied in the subsequent years to maintain the pH level near to that of year 1. A micronutrient mixture containing 9% Fe, 2.0% Mn, 2.0%

Cu, 0.5% B, 2.0% Zn and 0.5% Mo was applied at the rate of 45 mg kg^{-1} to both soils. The lime, fertilizers and micronutrients were thoroughly mixed throughout the 6.67 L of soil (about 8 kg) which was filled in 7-L plastic pots. The rates of fertilizer application were the same in all the five years of this study. The soil filled-pots after harvest were kept in the greenhouse until the next cropping season and used again in the subsequent years. The soil from each pot was taken out and thoroughly mixed with the As containing fertilizer, lime, and micronutrients, and returned to the same pot. The procedures employed in year 1 were repeated in the subsequent years.

2.4. Common Procedures for Both Experiments

In both experiments, procedures described below were carefully followed. Each treatment was replicated three times. The pots were randomised in the greenhouse to minimise the impact of location effects. About 20 barley seeds were sown in each pot which were thinned to 14 plants after germination. About 1.5 g of ryegrass seed was sown in each pot. The pots were watered immediately after sowing. The moisture content in the soils was maintained at about 15% by regular watering with deionized water throughout the growth period. Barley was harvested only once at maturity but ryegrass was harvested at the initiation of flowering, 5 times during the growth period. The fresh plant materials were oven-dried at 60 °C for 48 hr and the percent dry matter was calculated. The composite plant samples were taken to measure As concentration in both crops.

2.5. Chemical Analysis

Soil pH was measured in a 1:2.5 soil to water ratio. The soil suspension was allowed to stand overnight prior to pH determination by a pH meter. The concentrations of available P, K, and Mg were determined by ammonium lactate method (Egner *et al.*, 1960). The oxides of Fe and Al were determined by shaking 2 g soil and 100 ml of Na-dithionite solution for 12 hours. After filtration through a S&S filter paper, Fe and Al concentrations in the extract were determined in a 0.2% KCl solution by atomic absorption spectrophotometry. The level of As in both soils was below the detection limit (<0.3 mg kg^{-1}). Arsenic concentration in the crops was determined by the modified Gutzeit method described in Furman (1966). The method depends upon the evolution of arsine (AsH_3) by the action of hydrogen on As compounds under the catalytic action of Zn, the reaction taking place either in alkaline or acid solutions. The evolved arsine reacts with $HgCl_2$, on a impregnated filter paper, forming a coloured compound. From the length and intensity of the colour stain the amount of As is estimated by comparison with standard stains of arsine. Samples from replicates were pooled together for each treatment and analysed accordingly. Duplicate determinations of about 10% samples, selected randomly, were performed to assess the reproducibility of the method. All the chemical analysis data are reported on oven dry basis (105 °C).

2.6. Statistical Analysis

Analysis of variance was done by the Statview 1.03 (© 1988, Abacus Concept, Berkeley, California, U.S.A.) on a Macintosh computer.

3. Results and Discussion

3.1. Effect of Arsenite and Arsenate on Crop Yield and Arsenic Concentration

3.1.1. Crop Yield as Affected by As Forms

There was no statistical difference in ryegrass yield with the increasing rates of As over the 4 annual cuttings (data of the fifth cutting excluded due to the lack of chemical analysis for this cutting in year 1) and therefore only the yield sum is used for further discussion. The yield data for ryegrass and barley are presented in Tables II and III, respectively. In year 1, both arsenite and arsenate significantly decreased the yields of both crops but the reduction caused by arsenite was greater than that by arsenate (Tables II and III). The interaction effects of As valency states and the As application rate on ryegrass and barley yields were also significant. A marked yield difference between the two valency states was observed at the rates of 50 and 250 mg As kg^{-1}. At the rates of 10 mg As kg^{-1} or lower, the yield differences in barley were only minor but these differences in ryegrass, although small, were found to be consistent (Tables II and III). Although the interaction between As valency states and soil type was not found significant, the yield reduction in both crops due to arsenite application was observed at a lower rate of As application in the sand than in the loam soil.

The relatively higher inhibitory effect from arsenite on both crops in this study is consistent with the observations in the literature. The phytotoxicity of As is influenced more by their chemical forms than by their amount in given soil (Woolson *et al.*, 1971a). It is reported that arsenite is more soluble (Gulens *et al.*, 1979) and more toxic than arsenate (Sachs and Michael, 1971). Sachs and Michael (1971) further reported that arsenite was at least twice as phytotoxic as arsenate whether foliarly or root-applied. Arsenite is a well known thiol reagent combining rapidly with dithiol groups on proteins, and, hence an effective inhibitor of enzymes requiring free sulfhydryl groups (Webb, 1966). Arsenate, on the other hand, is a competitive inhibitor of phosphate (Jacobs and Keeney, 1970) and acts as an uncoupler of oxidative phosphorylation (Webb, 1966). Thus arsenate-treated plants are inhibited mainly by inadequate level of phosphorylated compounds, whereas arsenite-treated plants may suffer the immerdiate loss of activity of vital enzymes, including those necessary for oxidation phosphorylation. Furthermrore, arsenite reacts with sulphydryl enzymes leading to the production of complexes, membrane degradation and cell death. Arsenate action is, however, more subtle.

The residual effects of As valency states on ryegrass yield in years 2 and 3 were more marked than on barley yield (Tables II and III). The residual effect of As

TABLE II

Ryegrass yield as affected by As valency states, application rate, and soil type over 3 years (sum of 4 cuttings) in experiment 1

Source	Rate of As appl.	Year 1 Soil Sand	Year 1 Soil Loam	Year 2 Sand	Year 2 Loam	Year 3 Sand	Year 3 Loam
	(mg kg^{-1})			g pot^{-1}			
	0	101.2±0.9	116.9±2.3	88.0±1.5	113.2±5.6	66.5±3.0	86.5±2.7
As(III)	2	97.0±4.7	114.2±5.2	85.3±6.1	108.9±3.4	71.2±5.6	88.2±5.3
	10	95.6±1.3	114.5±3.9	84.9±0.4	99.6±7.7	70.0±1.4	83.6±3.2
	50	66.6±2.8	91.1±6.3	83.1±0.5	109.2±0.9	68.7±2.7	82.5±4.2
	250	2.6±0.2	24.5±13.9	4.2±1.3	94.0±4.6	3.6±0.3	89.3±4.2
As(V)	2	102.8±1.0	126.8±5.7	84.9±2.3	101.4±0.8	67.1±5.0	87.2±6.7
	10	101.9±2.2	119.5±3.0	82.9±2.7	106.3±1.3	72.8±1.1	90.0±2.7
	50	81.6±5.7	108.1±2.5	80.2±7.9	106.0±6.7	71.0±3.9	93.1±7.4
	250	9.0±2.5	42.8±4.0	45.3±8.6	95.0±7.9	31.3±6.8	86.3±5.3
LSD	Valency (V)	4.2***		2.5*		4.0***	
	Treatment (T)	6.7***		6.9***		6.2***	
	Soil (S)	4.2***		4.4***		4.0***	
	V*T	15.0**		15.5***		13.9**	
	V*S	ns		8.2**		ns	
	T*S	12.7*		15.5***		13.9**	

The LSD (the least significance level) marked with *, **, *** is significant at 95, 99, and 99.9% levels of significance, respectively, ns = not significant.

valency states persisted up to year 3 in ryegrass but it was more marked at the 250 mg kg^{-1} rate of As application. In barley, this effect was not consistent, and the barley yield appeared to be little affected by the valency states of As except at the 250 mg kg^{-1} rate in year 3. The interaction effects of As valency states with either soil type or As application rate were generally found to be significant in year 2 and 3 for ryegrass yield but these effects in barley were not found significant.

These results suggest that the two plant species differed somewhat in their response to As forms applied. The relative sensitivity of different crops to As forms has not been widely studied. It is, however, reported that arsenite is more soluble and mobile in the soil and thus more available to crops (Gulens *et al.*, 1979). Woolson (1973) studied phytotoxic response and crop uptake of arsenate by six vegetable crops and indicated that crops differed in their sensitivity to As application. Plant As concentrations corresponding to a 50% growth reduction were 0.7 mg kg^{-1}, in tomato fruit, 10 mg kg^{-1} in spinach leaf and up to 76 mg kg^{-1} in radish root. Deuel and Swoboda (1972a) also reported that soybeans were more

TABLE III

Barley yield as affected by As valency states, application rate, and soil type over 3 years in experiment 1

Source	Rate of As appl.	Year 1 Soil Sand	Year 1 Soil Loam	Year 2 Sand	Year 2 Loam	Year 3 Sand	Year 3 Loam
	(mg kg^{-1})			g pot^{-1}			
	0	71.1±8.3	92.6±1.5	37.2±4.2	63.8±0.6	33.2±3.1	53.8±3.9
As(III)	2	54.1±14.5	90.7±1.6	19.5±9.2	66.5±1.9	25.5±8.6	57.9±4.5
	10	57.8±6.2	92.3±1.6	28.1±1.3	60.3±3.3	27.2±4.6	61.5±0.2
	50	26.8±4.6	68.6±4.7	16.7±4.0	62.7±0.9	23.5±4.8	60.4±1.3
	250	1.0±0.8	5.1±5.1	1.9±0.8	16.9±4.5	0.8±0.2	16.1±4.6
As(V)	2	57.4±5.0	88.1±1.2	18.1±1.3	66.9±3.2	28.7±5.7	62.8±5.1
	10	57.9±8.0	87.5±1.5	22.6±6.1	61.3±0.5	23.4±3.6	64.9±2.2
	50	46.9±2.4	77.5±2.7	13.9±0.2	55.0±1.4	24.4±2.8	58.6±2.8
	250	5.2±1.7	15.1±4.5	3.5±2.0	10.8±2.7	2.4±2.2	23.1±2.7
LSD	Valency (V)	3.8**		1.8*		ns	
	Treatment (T)	7.9***		4.9***		5.7***	
	Soil (S)	5.0***		3.2***		3.6***	
	V*T	17.7**		ns		ns	
	V*S	ns		ns		ns	
	T*S	17.7*		11.1***		12.8***	

The LSD (the least significance level) marked with *, **, *** is significant at 95, 99, and 99.9% levels of significance, respectively, ns = not significant.

sensitive to As application than cotton. The results also suggest that the residual effect of As valency states on ryegrass yield persisted longer in the sand than in the loam soil. Thus the residual effects were dependent on As application rate, soil type, and plant species.

3.1.2. Arsenic Concentration as Affected by As Forms

Arsenic concentration in ryegrass and barley as affected by the two valency states of As in year 1 is presented in Figure 1. For ryegrass, the mean As concentration of the 4 cuttings is used as there were only minor differences among different cuttings. Arsenic concentration in barley was slightly higher when arsenite was used as As source compared to arsenate in year 1 and these differences were more marked at 50 and 250 mg As kg^{-1} rates of As application in the loam soil. The corresponding differences in the sand, although small, were quite consistent at rates higher than 10 mg As kg^{-1}. However, the trend as described above was not observed in years 2 and 3. The effect of As valency states on As concentration in ryegrass was

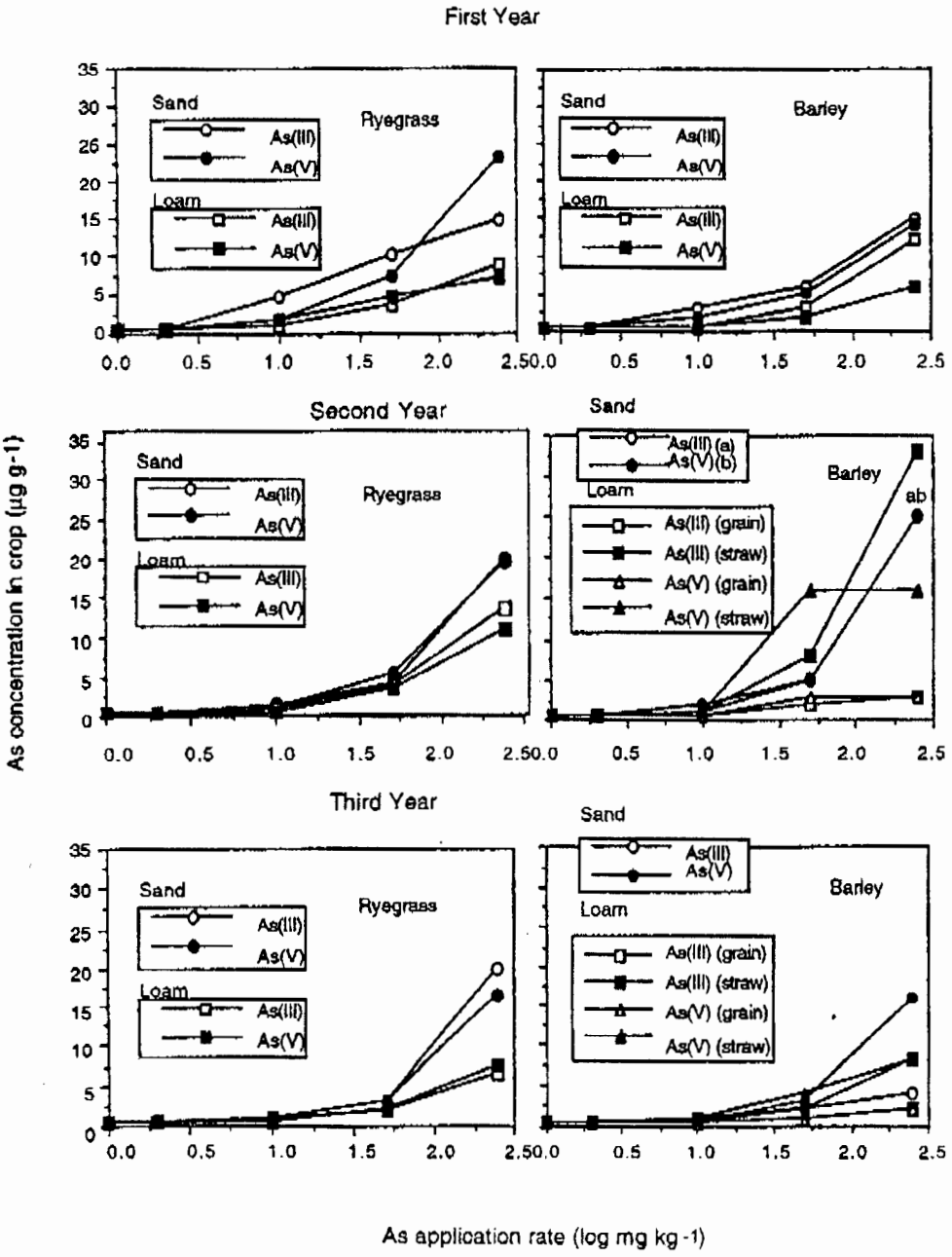

Fig. 1. Arsenic concentration in crop tissue as affected by As valency states, As application rates, and soil type.

TABLE IV

Yields (mean of two soils) at different rates of As application in year 1 in experiment 1

Application rates	Crop Barley	Ryegrass
(mg kg^{-1})	g pot^{-1}	
0	81.9a	109.0a
2	72.6a	110.2a
10	73.9a	107.9a
50	55.0b	86.9b
250	6.8c	19.7c
	$LSD_{0.05}$ = 13.1	$LSD_{0.05}$ = 15.7

The mean followed with the same letter in the same column are not significantly different at 95% level of significance using LSD multiple range test.

inconsistent at all the levels of As application in both soils. The results suggest that at the similar levels of dry matter or yield of the test crops, only minor differences in As concentration in crops between arsenite and arsenate sources were observed. It is reported that arsenite will be oxidised in normal agricultural soils to arsenate and therefore large differences between the effects of these forms of As on As concentration may not be expected.

3.1.3. *Effects of As Application Rates on Yield*

The yields of both crops decreased significantly at the rates of As application higher than 50 mg kg^{-1} (Table IV). At the rate of 250 mg As kg^{-1}, the yield reduction in the sand was as much as 97% for both crops, and in the loam soil 81% and 63% for barley and ryegrass, respectively. The growth reduction caused by As application has been observed by many investigators (Vandecaveye *et al.*, 1936; Jacobs *et al.*, 1970a; Woolson, 1973). Similar to the results of this study, Jacobs *et al.* (1970a) reported that potato yields decreased to 79 and 24% of the control yield at the rates of 90 and 360 mg As kg^{-1}, respectively. They also found yield reduction of snap bean and sweet corn with increased rate of sodium arsenite in a field study.

The regression analysis between crop yields and the As application rate in year 1 show that the yields of both crops were well correlated to the rates of As application (Table V). Woolson *et al.* (1973) observed that the corn growth was not linearly but sharply reduced at certain level of As application. Sandberg and Allen (1975) stated that a yield decrease in most cases could not be correlated with the total content of As in soils.

The residual effects of As applied in year 1 on the yields of both crops were

TABLE V

Linear regression between yield or As concentration in the crops and As application rate in year 1 in experiment 1

Condition	Yield[a]		As conc. in crop[b]	
	r^2	P value	r^2	P value
Ryegrass				
As(III) in sand	0.975	<0.001	0.768	>0.05
As(III) in loam	0.963	<0.001	0.959	<0.01
As(V) in sand	0.993	<0.001	0.988	<0.001
As(V) in loam	0.978	<0.001	0.834	<0.05
Barley				
As(III) in sand	0.760	<0.001	0.957	>0.01
As(III) in loam	0.985	<0.001	0.998	<0.001
As(V) in sand	0.915	<0.001	0.979	<0.01
As(V) in loam	0.992	<0.001	0.991	<0.001

[a] n = 15.
[b] n = 5.

also found significant in years 2 and 3 (Tables II and III). In year 2, barley yield started to decrease at the rate of 50 mg As kg^{-1} in the sand but a drastic decrease at the highest rate of 250 mg As kg^{-1} was observed in both soils and for both crops. Such yield decreases in year 3 were observed only at 250 mg As kg^{-1} rate for both crops, except ryegrass in the loam soil. These results suggest that the residual effects of As at the two highest rates persisted up to third year and that they lasted longer in the sand than in the loam soil.

3.1.4. Arsenic Concentration as Affected by As Rates

Arsenic concentration in both crops increased gradually with increased As application rates in year 1 (Figure 1). However, a marked increase in As concentration was observed at the rates of 50 mg As kg^{-1} or higher. Arsenic concentration in both crops was significantly correlated to As application rates in year 1 (Table V). Thoresby and Thornton (1979) observed a liner relationship between total As in the soil and the As concentration in barley grains, pasture herbage and lettuce. Sadiq (1986), on the other hand, found the As concentration in corn to correlate well with the water extractable As but not to the total As in calcareous soils. Similarly, Woolson (1973) found a linear relationship between As content in plants and the available As in soil in some test plants. The results in this study are somewhat similar to those of Sadiq (1986) and Woolson (1973).

The results in years 2 and 3 (Figure 1) were similar to those in year 1 in both crops. However, the decrease in As concentration in ryegrass was gradual from

year 1 to year 3. Such decrease in As concentration in barley (in the sand) in year 2 was not observed but the concentration tended to decrease in year 3. Lower yield reduction and decreased As concentration in both crops in years 2 and 3 seem to suggest that As availability to crops decreased over years. This may be caused by either its removal by crops or its fixation in soils with time. The fate of As in the soil is not well known, although in time it generally diminishes in toxicity. Vincent (1939) reported that a waiting period after application usually is the simplest method of alleviating toxic conditions, since soluble As became less toxic in the soil over a period of time. He further found that small fruit grow better on orchard soils taken out of production for 7 yr than on soils only 2 yr out of production. Similarly Woolson (1973) found growth of corn on the lakeland soil to improve with time at the 100 ppm As level because in this soil the water soluble-As level decreased and the Fe-As level increased after the 4 week incubation period. The clay fraction and iron oxides have frequently been implicated in the sorption of As by soils. The soils of this study contained appreciable amounts of Fe and Al oxides (Table I) and therefore part of the As applied may have been fixed by these oxides over time and became less available to plants. Jacobs *et al.* (1970) found the amount of As sorbed from solution increased as the free iron oxides content of the soils increased.

In years 2 and 3, As concentrations in barley grain and straw were investigated in the loam soil. Arsenic concentration in barley straw was much higher than that in barley grain (Figure 1). The higher the As application rates, the bigger the difference between grain and straw of barley. The decrease in As concentration from year 2 to year 3 was also observed but it was particularly marked for barley straw. The different parts of plants are known to accumulate varied level of As in tissues, with highest residues of As in roots, intermediate values in vegetative parts, and edible seeds and fruits containing the lowest levels of As (Woolson, 1973; Walsh and Keeney, 1975; Merry and Tiller, 1986). The results in this study are consistent with the findings of these other reports.

A large increase in As concentration in the crops at 50 and 250 mg kg^{-1} rates of As application resulted in a marked yield reduction, suggesting As in crops at these concentrations may have caused physiological damaged to plants. A level of As concentration in crops can be considered to be critical over which it will cause significant yield reduction. Therefore the critical As concentration in crops in this study are those at the As application rate of 50 mg kg^{-1} because maked yield reduction occurred at this rate of As application. The critical tissue levels of As for barley and ryegrass at this level of As application were 5.5, 2.5 and 8.7, 4.2 mg kg^{-1} in the sand and the loam soil, respectively.

3.1.5. Crop Yield and As Concentration as Affected by Soil Type

Generally, the yield reduction at any rate of As application was greater in the sand than in the loam soil (Tables II and III). However, the differences in yield reduction caused by As application in the two soils were greater in barley than in ryegrass

(Tables II and III). Similar effects of soil type on crop yields were also observed in years 2 and 3 (Tables II and III).

Soil texture is an important factor in determining the phytotoxicity of As added to soil. High rates of calcium arsenate application lead to aesenate residues which in turn caused growth reduction of cotton, soybean and rice plants in coarse textured soils but similar rates to fine textured soils did not produce toxic problems to plants (Reed and Sturgis, 1936). Similarly, Woolson (1973) observed that the decline in corn growth in the light textured soil occurred at a much lower application rate than that in the heavy textured soil. Jacobs and Keeney (1970) also found that the toxic effect of applied As on corn growth was more pronounced in a sand soil (7% clay) than in a silt loam soil (29% clay). Similar results were also obtained by Deuel and Swoboda (1972a) for cotton and soybeans grown in a fine sandy loam and a clay soil.

Arsenic concentration in both crops was significantly higher in the sand than that in the loam soil in all 3 yr (Figure 1). Akins and Lewis (1976) reported that water soluble As was inversely correlated to clay content. It was also shown that As sorption in the heavy textured soils was higher than in the light textured soils (Jacobs et al., 1970b; Liversey and Huang, 1981; Dudas, 1987).

The results of this experiment are in good agreement with those reported by others. As stated previously in this section, both clay and Fe oxide contents have been implicated in the sorption of As by soils. The loam soil in this study contained much higher contents of both clay and Fe oxides and therefore it is expected that the loam soil adsorbed more of the applied As. This was reflected in reduced toxicity of As and lower concentration of As plants grown in the loam soil as compared to the sand. Furthermore, the loam soil also contained many times higher organic carbon than the sand and the humic substances are also involved in As adsorption. Thunabalasingam and Pickering (1986) found As adsorption by humic materials to be dependent on pH. The maximum sorption of As (V) by the humics occurred at about pH 5.5, with the As(III) maximum being found at higher pHs and showing a more varied relationship between pH and type of humic material. The uptake mechanism appeared to be largely explained by the assumption that the humic were acting as anion exchangers. As the pHs became more alkaline the humic themselves became soluble and their ability to remove As from solution was decreased. During the whole growth period in this study, pHs were in the acidic range, being more acidic in the sand due to lower buffering capacity, hence adsorption of As by humic substances in the loam soil may also be responsible for the lower uptake of As in this soil.

3.2. Effect of Arsenic Contained in a NPK Fertilizer on Crop Yield and As Concentration

3.2.1. Crop Yield as Influenced by As Concentration in the Fertilizer

Ryegrass yields of different cuttings showed a similar trend with respect to As application. Thus, only the sum yields of the five cuttings are presented in Table

VI. Similarly, the yield of barley in Table VII is the sum of grains and straw because both plant parts were affected by the As application in a similar way. Yields of ryegrass or barley did not differ significantly among different As levels in the fertilizer and they also did not show any consistent trend (Table VI and VII). The results were similar in all the years except in year 4 where ryegrass yield decreased significantly at 3000 mg As Kg^{-1} level. These results show that As concentration in the NPK fertilizer, even as high as 3000 mg kg^{-1}, did not affect the yields of the crops tested in this experiment.

Although arsenite, which was incorporated in the fertilizer in this experiment, has been regarded to be highly toxic to crops (Sachs and Michael, 1971), the results of this study did not show such toxic effect. This may be because the As applied to the soils at the highest rate was equivalent to 1.9 mg kg^{-1} soil, which is much below the background concentration of As found in many soils (Fergussen, 1990). Davis *et al.* (1978) found 20 mg As kg^{-1} in barley tissues to be the critical level for growth reduction. The concentration of As in barley tissue in this experiment was lower than the critical value suggested by Davis *et al.* (1978).

3.2.2. Arsenic Concentration as Affected by As Concentration in the Fertilizer

Arsenic concentration in different cuttings of ryegrass showed a similar trend each year and the same was true for harvests of both crops in different years. Thus, the mean As concentrations of the 5 yr in both crops are used (Figure 2) for further discussion. The analysis of variance of As concentration in the crops was carried out by using the data of the 5 yr as 5 replicates. Arsenic level in the NPK fertilizer showed a significant effect on As concentration in both crops ($P < 0.001$). Arsenic concentration (mean of 5 yr) increased markedly at the rate of 3000 mg As kg^{-1} of the fertilizer (Figure 2), and the concentration was nearly 8 and 15 times higher for barley and ryegrass, respectively, than at the lowest level (10 mg As kg^{-1} of the fertilizer). At the rate of 100 mg As kg^{-1} of the fertilizer, the increase in As concentration in crops was only minor. Wiersma *et al.* (1986) reported that the mean As concentration of barley grown in uncontaminated soils in the Netherlands was 0.067 mg kg^{-1} on fresh weight basis. The As concentration of 0.12 mg kg^{-1} (Singh and Steinnes, 1976) and 0.13 mg kg^{-1} (Sandberg and Allen, 1975) in barley have also been reported. Barley grain contained As in the range of 3–18 ppb (Kabata-Pendias and Pendias, 1984). Compared to the As concentration in uncontaminated soils, the observed As concentration at the rate of 3000 mg As kg^{-1} fertilizer in this study was much higher and it exceeded the level considered safe from health point of view (Canadian Food and Drug Directorate, 1970).

Our results agree with Thoresby and Thornton (1979) who reported that the As concentration in barley grain increased with increased As concentration in the soil. Similar results were also reported by Woolson (1972) in corn when As was applied with single N, P, and K fertilizers or with compound NPK fertilizers. Woolson (1972) also found that P increased the As residues in the corn tissue and the NPK treatment resulted in the highest uptake of As by plants. However, it is interesting

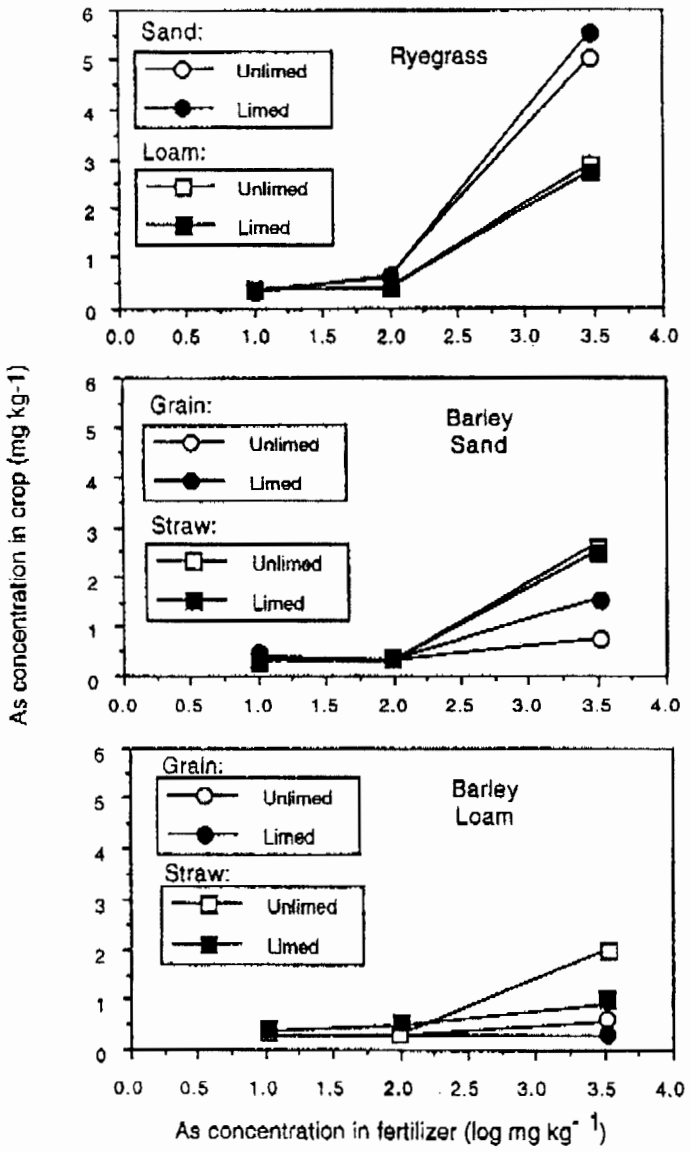

Fig. 2. Arsenic concentration in crop tissue as affected by As levels in the NPK fertilizer (mean of 5 yr).

to note that the application of the fertilizer containing 3000 mg As kg^{-1}, which was equivalent to As application at 1.9 mg kg^{-1} to soil, resulted in marked increase in As concentration in crops, whereas there was no such increase when As was applied at the same rate in the first experiment. The different results between the two experiments may suggest that As incorporated form in the fertilizer was more

TABLE VI

Effects of As levels in a NPK fertilizer, lime, and soil type on ryegrass yield (sum of the five cuttings) 5 years in experiment 2

Soil	Lime level	As conc. in fertilizer	Year I	II	III	IV	V
		(mg kg^{-1})			g pot^{-1}		
Sand	Unlimed	10	81.8±2.2	72.8±3.5	95.8±4.7	72.3±5.5	69.6±
		100	80.0±4.2	74.5±2.5	96.3±2.2	74.4±6.4	65.6±
		3000	75.6±1.1	68.9±4.9	97.1±0.9	63.2±4.1	66.3±
	Limed	10	84.4±1.1	75.2±1.9	99.9±2.0	70.9±2.8	69.1±
		100	80.4±2.2	71.7±0.6	100.0±1.7	68.0±2.2	67.4±
		3000	82.7±0.6	73.1±1.8	99.5±2.5	64.1±1.5	65.2±
Loam	Unlimed	10	75.0±2.6	66.1±3.6	93.7±1.9	66.2±0.8	60.0±
		100	76.0±4.5	67.8±2.5	95.8±2.2	64.6±4.5	58.3±
		3000	72.8±6.2	72.0±2.5	98.7±0.6	63.0±2.4	61.1±
	Limed	10	80.1±2.0	69.4±1.2	99.0±2.1	64.1±1.9	62.1±
		100	82.7±5.1	71.6±1.8	99.0±2.9	60.8±4.2	63.5±
		3000	78.9±1.9	70.4±1.6	95.8±2.5	59.1±2.3	61.3±
LSD	Treatment (T)		ns	ns	ns	4.5*	ns
	T*Lime		ns	ns	6.0*	ns	ns
	T*Soil		ns	6.6*	ns	ns	ns
	Soil		3.1**	2.7**	ns	4.5**	3.0**
	Lime		4.1***	ns	2.5**	2.5*	ns

The LSD (least significance level) marked with *, **, *** is significant at 95, 99, and 99.9% levels of significance, respectively. ns = not significant.

available to crops than its inorganic salts.

Arsenic concentration in either barley straw or ryegrass was higher than that in barley grains at the 3000 mg As kg^{-1} rate in the fertilizer (Figure 2). It is reported that vegetative plant tissues generally contain higher As than grains or fruits (Woolson, 1973; Walsh and Keeney, 1975; Merry *et al.*, 1986a).

The interaction effects of As level in the NPK fertilizer and soil texture on crop yields were not significant in most of the years (Table VI and VII). However, the interaction effects on As concentration in ryegrass were significant ($P<0.001$). Arsenic concentration in ryegrass in the sand was nearly twice as much as that in the loam soil at the highest rate of As application (Figure 2). A small increase in As concentration in ryegrass was also observed at 100 mg As kg^{-1} fertilizer in the sand. Similarly, soil texture also interacted significantly with the As levels in the NPK fertilizer on As concentration in barley grain ($P<0.01$) and straw ($P<0.01$). The marked differences of As uptake at the highest rate of application between soils

TABLE VII

Effects of As levels in a NPK fertilizer, lime, and soil type on barley yield (sum of grains and straw) over 5 yr in experiment 2

Soil	Lime level	As conc. in fertilizer	Year I	II	III	IV	V
		(mg kg^{-1})			g pot^{-1}		
Sand	Unlimed	10	31.5±5.1	36.7±12.7	15.3±7.8	54.7±13.5	51.9±3.4
		100	33.7±1.0	39.5±4.0	27.4±3.0	67.1±6.1	55.8±2.9
		3000	34.3±2.3	39.6±15.1	25.6±5.8	51.5±13.5	44.2±10.8
	Limed	10	49.6±2.7	62.6±1.9	60.8±2.2	55.7±1.9	51.9±0.5
		100	53.6±0.5	71.8±10.0	61.9±2.8	53.8±1.1	42.5±1.6
		3000	47.9±9.8	64.3±2.1	60.8±2.3	57.2±3.1	50.4±1.3
Loam	Unlimed	10	41.3±4.2	65.9±7.2	58.7±1.3	74.7±2.8	51.7±1.2
		100	41.7±4.6	61.1±2.5	52.6±7.3	77.3±2.8	57.3±0.6
		3000	41.1±2.1	59.1±2.9	52.3±4.0	73.5±3.4	57.0±3.0
	Limed	10	68.2±1.6	79.7±3.9	66.7±8.8	65.8±4.3	53.3±4.7
		100	68.9±0.1	74.7±3.2	72.8±2.4	65.8±1.0	54.0±1.0
		3000	68.0±2.1	81.2±2.4	68.7±3.6	68.2±2.2	56.7±2.2
LSD	Treatment (T)		ns	ns	ns	ns	ns
	T*Lime		ns	ns	ns	ns	11.9**
	T*Soil		ns	ns	ns	ns	9.7*
	Soil		4.9***	8.9***	6.1***	9.8***	4.8***
	Lime		4.9***	8.9***	6.1***	9.8***	4.8***

The LSD (least significance level) marked with *, **, *** is significant at 95, 99, and 99.9% levels of significance, respectively. ns = not significant.

indicate that the loam soil was able to decrease As uptake by the crops. These results are in general agreement with the previous experiment where both crops contained higher As in the sand than in the loam soil. The reasons given for differential uptake of As by plants from As(III) or As(V) in the two soils of different texture hold also true for As contained in the NPK fertilizers. It has also been reported by others (Jacobs and Keeney, 1970; Deuel and Swoboda, 1972; Woolson, 1973; Merry *et al.*, 1986a) that heavy textured soil generally decreased the availability of As to a greater extent than light textured soil, especially at high rate of As application. Woolson (1972) reported that at the low level of As application (10 mg kg^{-1}) it was difficult to detect difference between treated and untreated pots and that over 90% of the added As was fixed. This may be the reason that no marked difference in the As concentration was observed at the lower levels in this study.

3.2.3. Main Effects of Liming and Soil Type on Crop Yield and As Concentration
The effects of liming on crop yields were not consistent in all 5 yr. However, in the first 3 yr, significant higher crop yields were generally obtained in limed pots as compared to unlimed pots but effect of liming was more marked in barley than in ryegrass (Table VI and VII).

The effect of liming on As concentration in either of the crops was not significant ($P>0.05$). There were only minor changes in As concentration in both crops as a result of soil pH changes. Merry *et al.* (1986b) reported that As concentration in radish and silver beet were not changed significantly as pH changed and that it was insensitive to the changes of soil pH. Similarly, Baker *et al.* (1976) indicated that As concentration in potato tubers, snap beans, and cottonseed were unaffected by soil pH. These observations agree well with those in the present experiment. In contrast, it has been reported that the availability of As in soils is affected by changes in pH. In general there is an increase in As toxicity effects in plants as the soils become more acid, particularly at pHs below 5 when As-binding species such as fe and Al oxides become more soluble. However the uptake of As by plants may be increased at higher pH levels (Campbell *et al.*, 1985). Pot and field trials on the effect of applying sewage sludge, containing arsenate, to a sandy loam (pH6.0) and a calcareous loam (pH8.0) indicated enrichment factors that were 3.4 times greater in the lettuce and ryegrass grown on the calcareous loam. Woolson (1972) and Everett (1962) also reported that the increase in soil pH resulted in decreased available As and As uptake by the plants.

The effects of soil type on crop yields were significant in most of the years (Table VI and VII). Barley yield was significantly higher in the loam soil than in the sand, but ryegrass was opposite. The yield differences of barley between soils were similar to that in the first experiment as previously described.

Arsenic concentration in barley grain ($P<0.05$) or straw ($P<0.01$) and in ryegrass ($P<0.001$) were significantly lower in the loam soil than in the sand (Figure 2) but the effect was more marked at 3000 mg As kg^{-1} level. The rate of increase in As concentration was higher in the sand than in the loam soil. Similar to the previous experiment and to those by others (Deuel and Swoboda, 1972; Woolson, 1973; Merry *et al.*, 1986a), the As uptake by crops was lower in the heavy textured soil than in the light textured soil. The sorption capacity of a soil is affected by the texture, sesquioxides content and the presence of other interfering elements. Sand and silt fractions show little As sorption capacity due to low surface area and the predominance of quartz (Dickeas and Hiltbold, 1967) while the clay fraction is the main sorber (Jacobs *et al.*, 1970b). This is because As is adsorbed by minerals possessing exposed hydroxyl groups, such as kaolinite and Fe and Al oxides. The presence of Fe and Al oxides in soil is often correlated with clay minerals present and hence to soil texture. As stated previously loam soil contained higher amounts of Fe and Al oxides and may be able to reduce the uptake of As by crops.

TABLE VIII

Effects of supplemental P on yields of ryegrass and barley in two soil, with and without lime, over 5 yr

Crop	Lime level	Treatment	Year I	II	III	IV	V
					g pot^{-1}		
Ryegrass	Unlimed	As[a]	75.6±1.1	69.0±4.9	97.1±0.9	63.2±4.1	66.3±3.6
		As+extra P[b]	79.2±1.3	69.4±0.8	95.7±1.6	66.1±2.8	59.5±4.7
	Limed	As	82.7±0.6	73.7±0.6	99.5±2.5	64.1±1.5	65.2±3.4
		As+extra P	83.7±2.5	74.9±0.8	98.1±1.6	64.6±4.7	65.1±0.5
Barley	Unlimed	As	34.3±2.3	39.6±15.1	25.6±5.8	51.5±13.5	44.2±10.8
		As+extra P	39.1±1.7	59.3±6.5	62.1±1.9	55.3±2.6	48.9±3.7
	Limed	As	47.9±9.8	64.3±2.1	60.8±2.3	57.2±3.1	50.4±1.3
		As+extra P	55.3±1.2	69.7±7.6	62.1±1.9	53.1±4.0	47.6±3.8
LSD	Ryegrass	Treatment	2.0*	ns	ns	ns	ns
		Lime	4.4***	3.5*	2.3*	ns	ns
	Barley	Treatment	ns	12.2*	9.9***	ns	ns
		Lime	15.0***	12.2*	9.9***	ns	ns

The LSD (least significance level) marked with *, **, *** is significant at 95, 99, and 99.9% levels of significance, respectively. ns = not significant.

[a] Application of fertilizer containing 3000 mg As kg^{-1}.

[b] Extra P was applied at the rate of 51 mg kg^{-1}.

3.2.4. Crop Yield and As Uptake as Affected by Additional P Application

In the sand, an extra dose of P was added to the treatment containing 3000 mg As kg^{-1} fertilizer to study the influence of P on crop yields and As concentration in crop tissue. Slightly higher yield of reygrass was obtained with extra P application but the increase was not found to be significant in most of the years (Table VIII). In barley, the extra P application increased yields in years 2 and 3 (Table VIII) but no such increase was observed in other years in this experiment.

The effect of P on As concentration in ryegrass was significant ($P<0.05$) as the As concentration in ryegrass increased significantly ($P<0.05$) in P treated pots (Figure 3). The effect of P on As concentration in barley was not found to be significant (Figure 3). Woolson (1992) reported that P application increased the available soil As and As residues in corn tissues. On the other hand, P has also been reported to reduce As toxicity because As when applied as arsenate compete with P for the same sites in soils or transport systems (Dean and Robinson, 1947). Several authors have noted a reduction in effectiveness of As, as P levels increase, on a wide varity of crops (Benson, 1953; Woolson et al., 1973). Jacobs and Keeney (1970) reported that at the low level of applied As, P did not ameliorate As toxicity

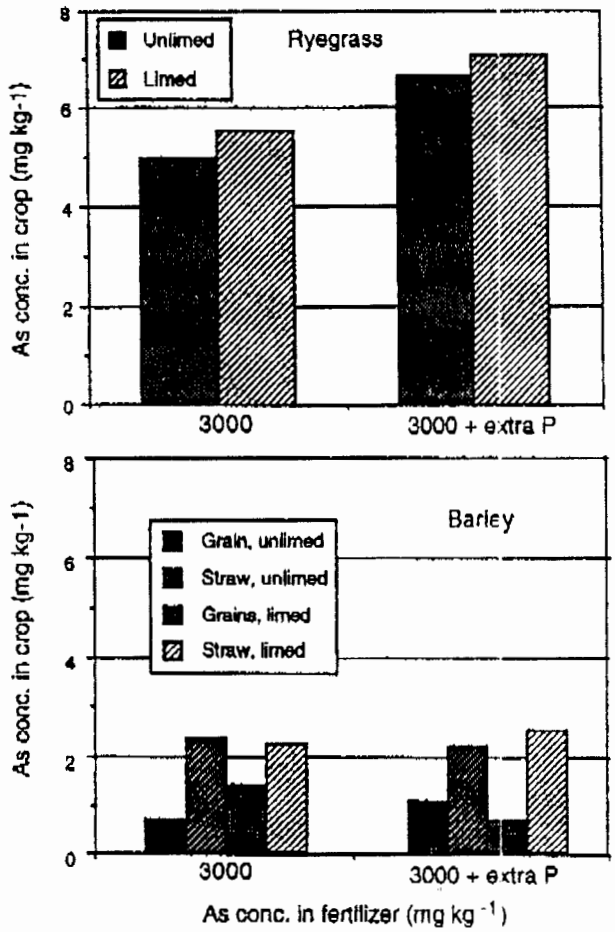

Fig. 3. Effect of additional P on As concentration in crop tissue.

to corn or influence As concentration in plant tissue. At the high As level, P did not influence As toxicity on the waupum soil, but enhanced As toxicity on the plainfield soil because the later soil has a relatively low As or P retention capacity. Addition of P could result in enhanced As toxicity due to displacement of arsenate by phosphate. These results have similarity to the observation made in the present study because addition of P to the sand which possesses low capacity to absorb P or As, increased the As concentration in plant tissue.

3.2.5. Effects of Repeated Application of the As Containing Fertilizer on Crop Yields and As Concentration

Although the mean yield varied considerably from one year to another, it did not show any consistent pattern of either increase or decrease as a result of repeated application of the As containing fertilizer (Figure 4). One may, thus, conclude that

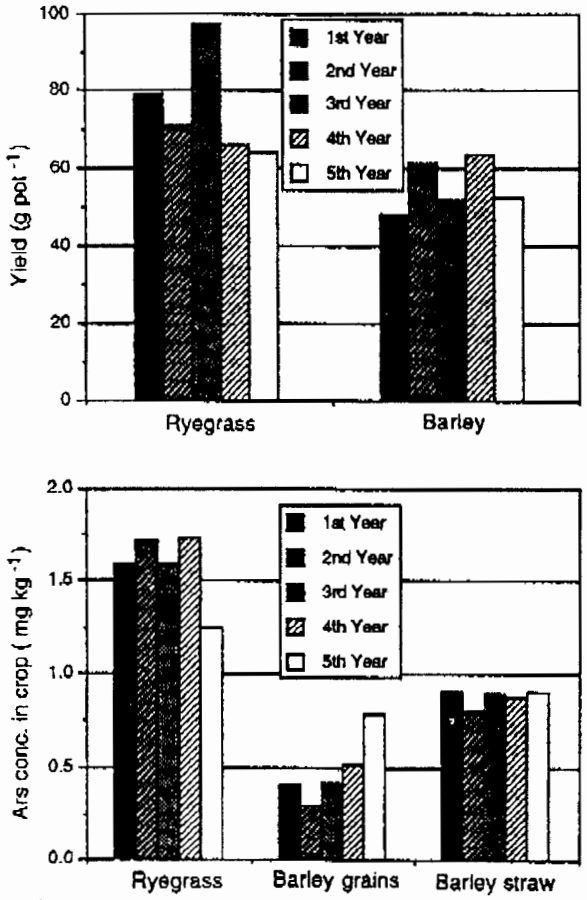

Fig. 4. Crop yield and As concentration in crop tissue (grand mean) as affected by the repeated application of As containing fertilizer.

the repeated application of the As containing fertilizer even at as high level as 3000 mg As kg^{-1} fertilizer did not seem to cause any inhibitory effect on plant growth.

Like yield, the As concentration in both crops was also not consistently affected by the repeated application of As containing fertilizer for a period of 5 yr. A slight tendency of higher As concentration in barley grain in the subsequent years was observed. The rates of As added through the fertilizers even at the highest level of 3000 mg As kg^{-1} fertilizer did not supply more than 1.9 mg As kg^{-1} soil, and the availability of the previously applied As decreased over time as observed in the first experiment with arsenite and arsenate sources of As. This may probably explain why the repeated application of As containing fertilizer did not increase the As concentrations in crop tissues.

4. Conclusions

Both arsenite and arsenate were found to decrease crop yields and increase As concentration in ryegrass and barley crops. Arsenite generally caused greater yield reduction than arsenate in both crops. The yield reduction due to As application was greater in the sand than in the loam soil because of higher As retention capacity of the later soil due to its higher content of Fe and Al oxides. At As application rates of 50 and 250 mg kg^{-1}, severe yield reduction was shown and the As concentration in both crops exceeds the health limit considered safe for food or fodder crops. The residual effect of As added in year 1 persisted up to year 3 but it was reduced with time. The results of the first experiment suggest that not only the application rate of As but also the As form, soil type, and the plant species grown should be considered while assessing the danger of As contamination of soils as well as of food and fodder crops.

The results in the second experiment suggest that the application of the As containing NPK fertilizer did not affect the crop yield but it increased the As concentration in both crops in both soils by several folds when applied at the rate of 3000 mg As kg^{-1} fertilizer. This rate of application increased the As concentration to a level considered unsafe for food and fodder crops. A direct comparison of the two experiments reveal that the availability of arsenite at the same level of application (about 2 mg kg^{-1}) to plants was higher when this source was incorporated in a NPK fertilizer than when it was applied separately. This implies that As contained in the fertilizer granule was either made more soluble during the manufacture precess or it was prevented to be adsorbed on soil particles by the competitive effect of phosphate.

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