1,2,4-oxadiazole (17 or 18). The only previous study of PMO metabolism was reported by Catanese et al. (1963). He stated that "the urine of rats treated orally with 1000 mg per kilogram of PMO disclosed the presence of small quantities of unaltered product and large quantities of hippuric acid and benzoylglucuronide. Diethylamine was absent as expected." Our investigation showed that urines from guinea pigs, rats, and dogs receiving PMO, or rats dosed with oxolamine citrate, did not show any significantly increased amount of hippuric acid or benzoylglucuronic acid when compared to controls. Also, we were unable to find the hydroxyethyl compounds 17 or 18, even though these were synthesized to aid identification.

We believe that all of the significant PMO metabolites have been identified. Based on the data in Table II, 88% of the radiocarbon in the urine of one of the male rats was accounted for among the identified metabolites. In another of the male rats, the total radioactivity of the breath, feces, urine, and body parts accounted for 91.7% of the PMO-^{14}C administered. The radioactivity not accounted for is due, no doubt, to either: (1) an erroneous determination of the $^{14}CO_2$ in the breath or (2) an erroneous estimate of the weight percents of blood, fat, and muscle in the body. These studies show that PMO appears to be rapidly excreted without persisting in tissues and organs.

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Supplementary Material Available: Figure 1, TLC autoradiogram of PMO-5-^{14}C; Figure 2, paper chromatographic presentation of the urinary metabolites of PMO-^{14}C in the male rat; Figure 3, TLC of the urinary metabolite fractions U1, U3, U4, and U5 of PMO-^{14}C; Figure 4, TLC separation of the biliary metabolites of PMO-^{14}C found in the male rat; I, comparison of the infrared and mass spectral data for natural and synthetic PMO metabolites; and II, GLC method for PMO (8 pages). Ordering information is given on any current masthead page.

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Fate of 2,2'-Dichlorobiphenyl-^{14}C in Carrots, Sugar Beets, and Soil under Outdoor Conditions

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2,2'-Dichlorobiphenyl-^{14}C was applied to soil (38 mg on a 60 × 60 cm area) in a box under outdoor conditions. In 1973 carrots and in 1974 sugar beets were grown. In the first vegetation period, 53.5% of the applied radioactivity was lost by volatilization, and in two vegetation periods 78.7%. In the first year, 49.5% of the radiocarbon in the treated soil layer was unchanged dichlorobiphenyl, 8.8% was soluble metabolites, and 41.7% was unextractable; in the second year, the percentage of unextractable residues increased to 74.3%. The presence of oxygenated metabolites in the extracts of soil and plants was confirmed by mass spectrometry. Carrot roots contained 0.240 ppm of 2,2'-dichlorobiphenyl and 0.012 ppm of metabolites; sugar beet roots contained <0.001 ppm of 2,2'-dichlorobiphenyl and 0.004 ppm of metabolites. The bioconcentration factor of 2,2'-dichlorobiphenyl in carrots was 2; metabolites were not concentrated. No bioconcentration of 2,2'-dichlorobiphenyl or metabolites was observed for sugar beets.

The occurrence of unchanged polychlorinated biphenyls (PCB's) in environmental samples including human food is well documented (summarized in Klein and Weisgerber, 1976). However, information on the possible presence of degradation products in agricultural soils and crops is very limited. PCB's are known to undergo various conversions under environmental conditions and to form phenols, together with other products, by irradiation (Hustert and Korte, 1974) or by metabolism in various organisms (Block

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and Cornish, 1959; Daly et al., 1972; Hutzinger et al., 1972, 1974; Yoshimura and Yamamoto, 1973; Wallnöfer et al., 1973; Moza et al., 1973, 1974; Herbst et al., 1976; Safe et al., 1974, 1975; Goto et al., 1974a,b, 1975; Berlin et al., 1975; Greb et al., 1975a,b; Kamal et al., 1976; Lay et al., 1975). Some of the phenols are reported to be more toxic than the parent compounds (Yamamoto and Yoshimura, 1973). Their formation has been observed in aquatic plants (Moza et al., 1973, 1974) but not in food crops. However, since PCB's are ubiquitous, they find their way into agricultural soils from which they may be taken up by crops and form unintended constituents in food. The objective of this paper, therefore, is to study the total balance of accumulation of a selected PCB isomer and its conversion products in agricultural soil and crops. 2,2′-Dichlorobiphenyl was selected as a representative of the lower chlorinated group known for rapid phenol formation in abiotic and biotic systems (Hustert and Korte, 1974; Moza et al., 1973, 1974; Herbst et al., 1976; Greb et al., 1975a; Kamal et al., 1976). As crops, carrots were chosen as a model for accumulators of lipophilic xenobiotics. In the second year, sugar beets were used as a model of a root crop with high water and low oil content.

EXPERIMENTAL SECTION

Apparatus. Packard liquid scintillation counters (Tri-Carb Model 3380 or 3375) with external standardization were used to measure the radioactivity in various extracts. Unextractable residues were determined by automatic combustion (Oximat, Intertechnique). Thin-layer chromatography (TLC) plates were scanned for radioactive substances on a scanner supplied by Berthold-Frieseke, GmbH, Karlsruhe.

Gas–liquid chromatographic (GLC) analysis was performed on a Packard unit, series 7400, with ECD and FID, fitted with a glass column (diameter 4 mm, length 2.0 m) packed with 1% OV-1 on Chromosorb W-AW-DMCS, 80–100 mesh, and nitrogen was used as a carrier gas. The radioactive substances were collected, after splitting 1:100, in anthracene tubes with the aid of an auxiliary Packard fraction Collector 852. A GLC–MS LKB 9000, from LKB-Producter, Bromma, Sweden, was used for the mass spectrometry.

Reagents. 2,2′-Dichlorobiphenyl-^{14}C (98.2% pure) was synthesized in this laboratory (Attar et al., 1973). A scintillation liquid based on dioxane was used for counting extracts and TLC zones. A toluene-based scintillator containing phenethylamine was used for counting $^{14}CO_2$. Silica gel G (Merck) was used for the preparation of TLC plates; ready made silica gel plates (Merck, 0.25-mm thick) were also used. For methylation of metabolites, diazomethane was freshly prepared from *p*-tolylsulfonylmethylnitrosamide and KOH in diethyl ether and then distilled.

Procedure. *Cultural Conditions of Plant Growing.* A water-resistant plywood box (60 × 60 × 60 cm) with a perforated base to drain the excess water, placed in a metal tray, was used to grow the plants. The outside of the box was wrapped in aluminum foil to prevent temperature increases from direct sunlight. The bottom of the box (2.5 cm) was layered with pebbles of nearly 2.5 cm diameter which in turn were covered with a layer of well-rotted turf. The box was filled with soil (160 kg) to 1 cm from the top and was kept in a large pit with the upper surface of the soil level with the surrounding ground; analysis of soil: coarse sand, 38.9%; fine sand, 36.9%; silt, 13.9%; clay, 10.3%; organic matter, 1.8%; pH 5.7. The soil was allowed to settle for nearly 4 weeks before treatment with 2,2′-dichlorobiphenyl-^{14}C and sowing. Fertilizers (KH_2PO_4 and calcium ammonium nitrate) were applied as in agriculture practice.

In 1973, 2,2′-dichlorobiphenyl-^{14}C (specific activity 1.08 mCi/mmol, 38 mg on 60 × 60 cm) in acetone was applied dropwise on the soil surface and was incorporated to a 10-cm depth resulting in about 1 ppm in dry soil. Carrot seeds ("Rote Riesen") were sown in three rows. Air temperature (maximum weekly, average, 32 °C; minimum weekly, average, 9 °C) and rainfall (239 mm) were recorded during the normal vegetation period (4 months).

The following year (1974), sugar beet seeds were sown in the same soil (used for the experiment with carrots). After 1 month of germination, only four sugar beets were allowed to grow in the box (the others were harvested prematurely and stored at −20 °C until analyzed). As usual, air temperature (26 °C/7 °C) and rainfall (489 mm) were recorded; vegetation period, 6 months. During both vegetation periods, the water drained from the box was collected and checked for radioactivity.

Working Up of Plant Material, Soil, and Leaching Water. Normal growth and yield of plants were observed at the time of harvest. The roots and leaves were analyzed separately. Soil samples (approximately 1 kg each) were taken at depths of 0–10, 10–20, 20–30, and 30–40 cm immediately after the harvest. These were stored at −20 °C until analyzed. The moisture content of soil samples was determined by drying to constant weight in a vacuum desiccator at room temperature.

The plant samples were homogenized and extracted continuously with methanol for 48 h. Soils were soxhleted with methanol for 48 h. From the radioactivity unextractable by this method, an additional part was recovered by heating the soils with 6 N HCl in methanol for 8 h. Acetonitrile, and various compositions of acetonitrile with water, failed to extract a reasonable amount of the unextractable radioactivity. The leaching water was acidified with HCl and extracted with ether.

The radioactivity in extracts and in leaching water was determined by counting samples of 100, 200, and 500 μl in a liquid scintillation counter. The data obtained were corrected by counting blanks of inactive extracts prepared in the same manner as the active ones. Unextracted radioactivity in soil and plants was determined by the combustion of 200-mg samples after extraction and drying in a vacuum desiccator at room temperature.

For the determination of 2,2′-dichlorobiphenyl and its conversion products, the individual extracts were concentrated in a rotary evaporator. The extracts were subjected to TLC analysis on silica gel plates in benzene/ethyl acetate (9:1). Zones of 1 cm were removed from the plates, and the radioactivity of each zone was counted in a liquid scintillation counter.

Isolation and Identification of the Conversion Products. The methanolic extracts of *soil* samples (0–10, 10–20, 20–30, and 30–40 cm) were combined and concentrated. The combined concentrated extract was separated into four radioactive zones on preparative silica gel plates (20 × 20 cm, 24 g of silica gel) using benzene/ethyl acetate (9:1). Zone IV which moved to the front on the plate was found to be 2,2′-dichlorobiphenyl upon TLC and GLC comparison with an authentic sample.

Zone III on further TLC analysis was resolved into three radioactive substances (plate run first with 25% benzene in *n*-hexane and then with benzene). The main metabolite (80% of this zone, R_f 0.6) was methylated with freshly prepared diazomethane. The methylated product (R_f 0.53 in benzene/hexane, 1:3), after further purification on TLC, was subjected to GLC–MS analysis. Another substance

Table I. Distribution of Radioactivity in Carrots, Soil, and Sugar Beets (in Percent of Applied Radioactivity) after Soil Treatment with 2,2′-Dichlorobiphenyl-^{14}C

Expt	Soil 0-10 cm	Soil 10-20 cm	Soil 20-30 cm	Soil 30-40 cm	Leached water	Carrots/ sugar beets	Leaves	Weeds	Total
With carrots (1st year)	24.1	17.1	3.2			1.3	0.6	0.2	46.5
With sugar beets (2d year)	15.2	3.8	1.7	0.4	0.2	<0.1	<0.1	<0.1	21.3

Table II. Residues of 2,2′-Dichlorobiphenyl-^{14}C and Metabolites in Carrots and Soil (Parts per Million Equivalent to 2,2′-Dichlorobiphenyl), TLC, Solvent 10% Ethyl Acetate in Benzene

Sample	Zone I (origin) (conjugates)	Zone II (not identified)	Zone III (monohydroxy metab.)	Zone IV (front) (PCB)	Unextract. metab.[a]	Total residue
Soil (0-10 cm)	0.008	0.003	0.010	0.118	0.100	0.239
Soil (10-20 cm)	0.005	0.001	0.005	0.089	0.069	0.169
Soil (20-30 cm)	0.001	<0.001	0.001	0.009	0.020	0.032
Soil (30-40 cm)	n.d.[b]	n.d.	n.d.	n.d.	n.d.	n.d.
Carrots	0.002	0.003	0.002	0.240	0.005	0.252
Leaves	0.074	0.004	0.012	0.108	0.033	0.231
Weeds (dried)	0.100	0.045	0.123	0.604	0.092	0.964

[a] Unextractable with organic solvents. [b] n.d. = none detected.

in this zone (5–10%, R_f 0.35) was methylated, also, and subjected to GLC–MS analysis.

Zone II of the extract, on further TLC analysis, was found to be a mixture of radioactive substances whose identification by instrumental analysis was impossible because of insufficient quantities.

The polar fraction (zone I) was hydrolyzed with 9 N H_2SO_4 at 70 °C for 8 h, diluted with water, and extracted with ether. The hydrolysate on TLC examination was found to be a mixture of substances. The major one (70%, R_f 0.6, plate run first with 25% benzene in *n*-hexane and then with benzene) was purified by repeated TLC, methylated with CH_2N_2, and subjected to GLC–mass spectrometry.

The methanol extract of *carrots* contained an inadequate amount of conversion products and was not investigated for metabolites. For isolation of the metabolites from leaves, the methanolic extract was concentrated and analyzed like the soil extracts. Isolation and identification of conversion products from *sugar beets* failed due to very small residues.

RESULTS AND DISCUSSION

Balance of Total Radioactivity. In the first year of this study (1973), 44.4% of the total applied radioactivity was found in the soil while 2.1% was taken up by carrots and weeds (Table I). The radioactivity in the soil was dispersed to a 30-cm depth; no radioactivity was found in the deeper soil layer and in the leaching water drained from the bottom of the box (>40 cm depth, detection limit 0.001 ppm). The total amount recovered was 46.5%; that means that more than half of the applied radioactivity was lost by volatilization (53.5%).

The loss of radioactivity is not due to the application method, since the compound solution was not applied by spraying, but was added dropwise to the soil and incorporated immediately. The volatilization is rather due to abiotic physical factors and/or to microbial influences. The chemical identity of the volatilized radioactivity could not be established. Although, by trapping methods, this is principally possible, such a procedure was not undertaken, since it would disturb the natural outdoor conditions which are the topic of this paper. It is possible that the volatilized radioactivity includes the unchanged parent compound which has a high vapor pressure and a low water solubility (1.5 mg/l.); also, PCB's were detected in many air samples (see, e.g., Bidleman and Olney, 1974). According to our knowledge, nothing is known on the volatilization of phenolic derivatives that are formed by irradiation or by metabolism as discussed in the introductory statement and in the following sections. The major residues remained at the application site (soil, 0–10 cm depth).

In the second year (1974), 21.1% of the applied radioactivity was found in soil, 0.2% in the leaching water, and less than 0.1% in sugar beets and weeds (Table I). With a lapse of 1 year, radioactivity had reached the bottom of the box (40 cm depth). The total recovery was 21.3%, corresponding to a volatilization of 78.7%.

The uptake of radioactivity by carrot roots (1.3% of the applied radioactivity) was much higher than by sugar beet roots (less than 0.1%). The difference is greater than expected from the difference between the corresponding soil concentrations. This is in good agreement with the well-known fact that carrots, due to their oil content, tend to take up lipophilic soil constituents.

Conversion and Residues. The radioactivity recovered from soils and plants consisted of unchanged 2,2′-dichlorobiphenyl, of soluble metabolites, and of radioactive residues unextractable with organic solvents. In the upper soil layer (0–10 cm depth), one growing season after treatment, 49.5% of the radioactivity present was unchanged 2,2′-dichlorobiphenyl, 8.8% was soluble metabolites, and 41.7% was unextractable residues. In the second year, the unextractable residues increased to 74.3%.

The soluble metabolite fraction was separated by TLC into several metabolite zones. Tables II and III show the concentrations of these metabolites in carrots, sugar beets, and soils, together with 2,2′-dichlorobiphenyl and unextractable residues. For the plant samples, parts per million are based on fresh weight; for soil samples, parts per million are based on dry weight determined by drying to constant weight in a vacuum desiccator at room temperature.

Identification of Metabolites. Identification of metabolites was carried out with soil extracts of both years and with carrot leaf extract. Metabolite zone III in Tables

Table III. Residues of 2,2′-Dichlorobiphenyl-^{14}C and Metabolites in Sugar Beets and Soil (Parts per Million Equivalent to 2,2′-Dichlorobiphenyl), TLC, Solvent 10% Ethyl Acetate in Benzene

Sample	Zone I (origin) (conjugates)	Zone II (not identified)	Zone III (monohydroxy metab.)	Zone IV (front) (PCB)	Unextract. metab.[a]	Total residue
Soil (0-10 cm)	0.005	0.001	0.004	0.029	0.112	0.151
Soil (10-20 cm)	0.001	0.001	0.001	0.005	0.029	0.037
Soil (20-30 cm)	0.001	<0.001	0.001	0.006	0.009	0.017
Soil (30-40 cm)	<0.001	<0.001	<0.001	0.003	0.004	0.008
Sugar beets	0.001	<0.001	<0.001	<0.001	0.002	0.004
Leaves	<0.001	<0.001	<0.001	<0.001	0.006	0.007
Weeds (dried)	0.016	0.001	0.001	0.002	0.186	0.206
Leached water	0.001	<0.001	<0.001	<0.001	0.001	0.002

[a] Unextractable with organic solvents.

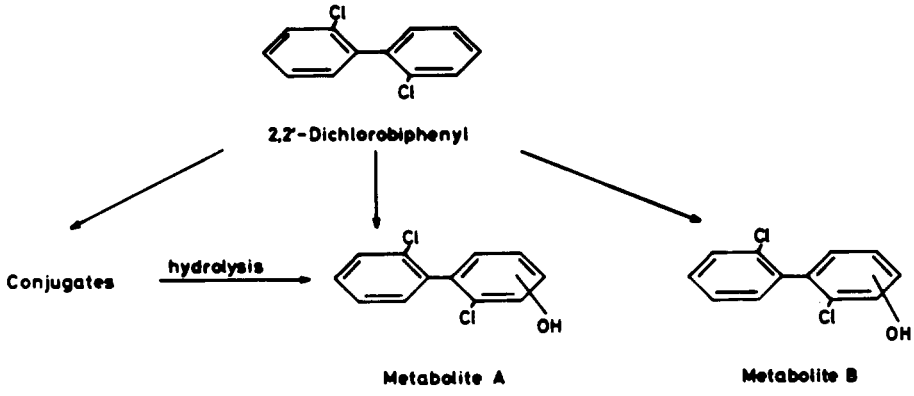

Figure 1. Conversion of 2,2′-dichlorobiphenyl in soil and carrots.

II and III of both *soils* contained, as the major component, an acidic substance which was identified by GLC/mass spectrometry after methylation (metabolite A). The mass spectrum of this compound was easily identified by the characteristic isotope distribution pattern for two chlorine atoms at a molecular ion at m/e 252 ($C_{13}H_{10}OCl_2$). The fragments are at 237 ($M^+ - CH_3$), 217 ($M^+ - Cl$), 209 ($M^+ - CH_3 - CO$), 202 ($M^+ - Cl - CH_3$), 174 ($M^+ - Cl - CH_3 - CO$), 173 ($M^+ - CH_3 - CO - HCl$), and 139 ($M^+ - Cl - CH_3 - CO$). These fragments suggest that one atom of oxygen is introduced into the molecule giving a hydroxy product which is methylated by diazomethane to methyl ether. The mass spectrum of this hydroxy derivative was identical with the spectrum of a metabolite of 2,2′-dichlorobiphenyl from water plants (Moza et al., 1974). The metabolite constituted about 80% of zone III. Another metabolite of this group (metabolite B) amounted to 5% in the first year and to 10% in the second year. It had the same TLC behavior as another isomer of a monohydroxy derivative of 2,2′-dichlorobiphenyl which has been reported earlier (Moza et al., 1974). The mass spectrum was very similar to that of metabolite A, but intensities were different, as well as R_f values and GLC retention times. Zone II consisted of a mixture of compounds insufficient for further investigation.

The polar fraction (zone I) was a group of conjugates which, upon hydrolysis, were shown by GLC/MS analysis to contain, among other unidentified products, an oxygenated compound (major one) of 2,2′-dichlorobiphenyl. TLC and GLC proved it to be identical with metabolite A from zone III of this extract.

The metabolites isolated from *carrot leaves* were a free phenol in zone III, identical with metabolite A from soil, and conjugates of the same phenol. *Carrot roots* contained only about 5% of the radioactivity present as soluble and unextractable metabolites. These could not be identified due to the small amount, but logically they should be the same as those in the carrot leaves. In respect to food residues, they are of very little significance since they represent only 0.012 ppm. It may be concluded that the only important residue in carrot roots is unchanged 2,-2′-dichlorobiphenyl (0.240 ppm).

The metabolites in *sugar beets* also could not be identified due to the small amounts. In sugar beets, neither metabolites nor 2,2′-dichlorobiphenyl itself represent significant residues; altogether they amount to less than 0.01 ppm (2,2′-dichlorobiphenyl < 0.001 ppm, metabolites 0.004 ppm). It is noteworthy that, in contrast to carrots, the hydrophilic and unextractable residues are higher than the unchanged 2,2′-dichlorobiphenyl. This difference may be due to differences in composition of the two crops.

The conversion of 2,2′-dichlorobiphenyl to identified metabolites is shown in Figure 1.

Accumulation of Residues from Soil in Plants. 2,2′-Dichlorobiphenyl is known to be accumulated from water by flora (Moza et al., 1974) as well as by fauna (Herbst et al., 1976); the concentration factors observed were between 290 and 800. The figures in Tables II and III, however, indicate that carrots, in spite of their high lipoid content, accumulate the unchanged 2,2′-dichlorobiphenyl from soil only by the factor 2, and the metabolites are not biomagnified at all. Sugar beets do not show any bioconcentration of 2,2′-dichlorobiphenyl or metabolites.

CONCLUSION

2,2′-Dichlorobiphenyl is volatilized rapidly from soil. In soil, as well as in carrots and sugar beets, it is converted to phenolic substances; the only important residue is the unchanged 2,2′-dichlorobiphenyl in carrot roots (0.240 ppm when the soil residue is 0.118 ppm). However, PCB residues in agricultural practice are expected to be lower. Thus, the danger of contamination of foods of vegetable origin by lower chlorinated PCB's will probably exist only for heavy contaminated soils. For higher chlorinated PCB's, further work must be done.

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Multielement Uptake by Vegetables and Millet Grown in Pots on Fly Ash Amended Soil

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Forty-two elements were determined in beans, cabbage, carrots, millet, onions, potatoes, and tomatoes grown on potted soil amended with 10% by weight of fly ash. Thirty-two elements were present at higher total concentrations in the fly ash than in the soil. As, B, Ca, Cu, Fe, Hg, I, K, Mg, Mo, Ni, Sb, and Se were higher in concentration in the edible portions of at least three of the crops grown on fly ash amended soil as compared to the control crops. The extent of plant absorption of selenium was roughly proportional to the rate of application of fly ash. The effect of the fly ash amendment on crop yields was variable.

It has been estimated that about 29 million tons of fly ash will be produced by coal-burning, electric power-generating plants in the United States during 1975 (Brackett, 1970). Fly ash has been used as an additive to concrete and ceramics (Buttermore et al., 1972), as a filtering aid in the processing of municipal sewage (Lukz, 1972), and as a base material in roadbeds ("Ash at Work", 1969). Since these applications consume only a small fraction of the total production its possible use in agriculture has been investigated. In the past the bottom ash from coal burned in homes was commonly put on gardens and, to a small extent, the public uses fly ash, privately hauled from power plants, for that purpose today. Fly ash has been added as an alkaline amendment to coal mine spoils and refuse banks to permit their reclamation for plant growth to stop erosion (Adams et al., 1972). It has been used in several areas in England to reclaim land for the growth of forage and pasture crops (Barber, 1974). The use of fly ash to improve soils has been reviewed (Plank and Martens, 1973).

Analysis of fly ashes (Davison et al., 1974; von Lehmden et al., 1974) indicates that a great number of essential and toxic elements may be present. Limited data have been obtained on the absorption of elements by forage grown on fly ash amended mine spoils (Adams et al., 1972). It has been added to soil to correct plant deficiencies of boron, molybdenum, phosphorus, potassium, and zinc (Doran and Martens, 1972; Martens, 1971; Martens et al., 1970; Schnappinger et al., 1975). In a recent paper (Furr et al., 1975), 35 elements were determined in fly ash, sweet clover grown on it, and tissues of guinea pigs fed the clover as 45% of their diet for 90 days. Several elements including selenium and rubidium were found to be greatly elevated in the fly ash grown clover and the tissues of guinea pigs consuming the clover as compared to the controls. The objective of the work reported here was to study the extent of absorption of a range of elements by plants representing major classes of edible garden crops

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