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Lead Content of Vegetables, Millet, and Apple Trees Grown on Soils Amended with Colored Newsprint

Don C. Elfving, Carl A. Bache, and Donald J. Lisk*

Apple trees, vegetables, and millet were grown successively for 2 years in pots in an acid or a neutral soil in which was incorporated 10% by weight of pulverized colored magazines and newsprint. Analysis of harvested mature plant material indicated that small quantities of lead may be absorbed by plants when grown on such paper-amended soils.

Millions of tons of waste paper result annually in the United States. The material is disposed of by incineration, in landfills, and recycling for various uses. Burning waste paper is being prohibited in many communities. Also areas suitable for landfills are dwindling. Since recycling of waste paper presently utilizes only a relatively small percentage of the total available, other uses for it have been proposed. One such possible use is as a soil mulching material in agriculture.

A toxic element of concern in paper is lead which is used as a dye in the inks. Its concentration may range up to about 500 ppm in colored newsprint (Serum et al., 1973; Heffron et al., 1977). In the work reported, a number of vegetable species, millet, and apple trees were grown in potted soils amended with colored newsprint. Lead was then determined in the edible harvested plant material to learn the possible extent of absorption of lead as a function of time and soil pH.

EXPERIMENTAL SECTION

The colored paper used derived from magazines, rotogravure sections of newspapers, brochures, and catalogs. Staples were removed, and about 75 kg of the paper was pulverized in a hammer mill equipped with a 0.32-cm mesh sieve. The paper was thoroughly mixed by quartering. The soils used were a Mardin silt loam (Typic Fragiochrept, coarse-loamy, mixed, mesic),pH 5.6, with an exchange capacity of 15.6 mequiv/100 g sampled near Dryden, New York, and a Teel silt loam (Fluvaquentic Eutrochrept, coarse-loamy, mixed, mesic), pH 7.2, with an exchange capacity of 13.9 mequiv/100 g. The Teel soil originated from alluvial deposits in the vicinity of Varna, New York. The soils were air-dried, sifted through a 2-mm screen, and mixed by quartering. Ten percent (w/w) of the paper was thoroughly mixed with each of the soils in a cement mixer. Ten percent (w/w) pulverized virgin bond paper containing no ink was similarly mixed with the above soils to serve as controls.

The crops used were 'Empire' and 'McIntosh' apple (*Malus domestica* Borkh.) on M-7A rootstock, 'Tendercrop' bush bean (*Phaseolus vulgaris*), 'Golden Acre' cabbage (*Brassica oleracea* var. *capitata*), 'Scarlet Nantes' carrot (*Daucus carota* var. *sativa*), Japanese millet (*Echinochloa crusgalli* var. *frumentacea*), '1620 Pedro' onion (*Allium cepa*), 'Katahdin' potato (*Solanum tuberosum*), and 'New Yorker' tomato (*Lycopersicon esculentum*). The crops were seeded in pots with the exception of apple, cabbage, onion, and tomato which were planted as transplants. All of the crops were grown in 7.6-L plastic pots except apple and potato which were grown in 11.4-L pots. The weights of the growth media contained in the 7.6- and 11.4-L pots were, respectively, 5.8 and 9.3 kg for the Mardin soil and 6.8 and 11.5 kg for the Teel soil. The numbers of plants grown in each pot were apple, 1; bean, 3; cabbage, 1; carrots, 10; millet, 5; onion, 3; potato, 1; and tomato, 1. All treatments were replicated four times. The plants were fertilized weekly with 1000 mL (1500 mL for the 11.4-L pots) of a solution containing reagent grade KH_2PO_4 (0.001 M) and KNO_3 (0.005 M) (Hoagland and Arnon, 1950). All plants were watered as necessary.

At maturity the crops were harvested. Only the edible portions were collected for the determination of lead. Since

Departments of Pomology (D.C.E.) and Food Science (C.A.B., D.J.L.), Pesticide Residue Laboratory, New York State College of Agriculture, Cornell University, Ithaca, New York 14853.

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Table I. Total Lead Content of the Soils and Paper

sample	lead, ppm, dry wt
Mardin silt loam, pH 5.6	15.0
Teel silt loam, pH 7.2	13.5
colored paper	567
bond paper	0.2

no apple fruit was produced, only leaves and twigs were sampled. With millet the plants were separated into grain as one sample and combined stems and leaves as the other. Prior to analysis all crop portions were rinsed with distilled water to remove adhering dust. Carrots, onions, and potatoes were brushed, rinsed, and peeled. The total, respective, replicated, edible plant portions were combined and subdivided by homogenizing in a blender, chopping in a food cutter, or dry milling. Fresh plant material was freeze-dried in polystyrene containers, mixed, and subsampled for analysis. Samples of the soils and paper were also taken for the determination of lead.

A second planting of the vegetables and millet was made in the same pots of growth medium. After harvesting the first crops, the pots of medium were stored in an unheated greenhouse during the winter to simulate field practice. The following spring, the contents of each pot were dumped out, the lumps broken up, and the material (plus partially decomposed roots) was again placed in the respective pot and the same crop grown a second time. The pH values of the various growth medium at the end of the 2-year plant growth studies were: Mardin silt loam containing bond paper (control), 5.7; Mardin silt loam containing colored paper, 5.5; Teel silt loam containing bond paper (control), 7.1; Teel silt loam containing colored paper, 7.3.

The determination of lead was performed by dry ashing the samples up to 475 °C, followed by analysis using conventional stripping voltammetry with a Princeton Applied Research Corp. Model 174 polarographic analyzer (Gajan and Larry, 1972). The determination of pH was made by the method of Peech et al. (1953).

RESULTS AND DISCUSSION

The total lead content of the soils and paper are listed in Table I. The high lead concentration in the colored newspaper (567 ppm) is in agreement with the lead content of such paper reported earlier (Heffron et al., 1977). This value for lead in colored printed paper is not surprising since it has been reported that among the multicolor letterpress inks used in magazines, the yellow contained 29 000, red 4100, blue 445, and black 275 ppm of lead (Hankin et al., 1973).

The lead content of the harvested crop material is shown in Table II. Wilcoxon's signed rank test (Steele and Torrie, 1960) for detecting real differences between paired treatments showed that the differences in lead concentration between the colored paper-grown and control crops were significant ($p < 0.05$) for all treatments except the crops grown during the first year on the pH 7.2 soil. The relatively high concentration of lead (3.00 ppm) in the millet grain in the latter treatment is believed to be due to inadvertent contamination. Repeated analyses of subsamples of it verified this elevated level of lead.

The uptake of lead by plants has been studied by others. Raising soil pH has been reported to decrease the availability of lead to plants (Cox and Rains, 1972; John and Van Laerhoven, 1972; Zimdahl and Foster, 1976; John, 1972; Miller et al., 1975a,b). The addition of organic matter to soil has been reported to decrease the availability of lead to corn (Zimdahl and Foster, 1976) but to show no effect in the case of lettuce and oats (John, 1972). Lead

Table II. Lead[a] Concentration (ppm, dry wt) in Harvested Plant Material Grown 2 Years in Succession on Potted Soils Amended with 10% by Weight of Colored Newsprint

	soil pH 5.6		soil pH 7.2	
crop	control	paper	control	paper
	First Year Crops			
apple leaves (Empire)	5.30	6.62	6.81	5.04
apple leaves (McIntosh)	3.99	5.25	3.52	5.09
beans	1.13	0.93	1.21	1.02
cabbage	1.01	1.26	0.86	1.67
carrots	1.19	1.48	0.79	1.54
millet straw	1.41	1.85	1.92	1.22
millet seed	1.16	1.35	3.00	1.00
onions	0.41	0.47	0.43	0.69
potatoes	0.21	0.22	0.23	0.25
tomatoes	0.47	0.32	0.58	0.32
	Second Year Crops			
apple leaves (Empire)	5.50	7.71	6.04	6.27
apple leaves (McIntosh)	6.53	8.01	5.96	7.42
apple twigs (Empire)	1.19	1.60	1.04	1.16
apple twigs (McIntosh)	1.04	0.91	1.10	1.22
beans	0.84	0.89	0.75	1.30
cabbage	1.18	1.15	1.24	0.84
carrots	0.85	1.34	0.49	0.70
millet straw	0.96	1.46	0.81	1.00
millet seed	2.20	3.13	1.11	1.82
onions	0.27	0.32	0.37	0.25
potatoes	0.11	0.13	0.06	0.13
tomatoes	0.32	0.24	0.21	0.24

[a] Differences were significant ($p < 0.05$) using Wilcoxon's signed rank test for all treatments except the crops grown during the first year on the pH 7.2 soil.

absorption has been reported to be reduced in corn Miller et al., 1975a) and tree seedlings (Rolfe, 1973) but to be unaffected in soybeans (Miller et al., 1975a) by an increase in available soil phosphorus. The nature of the crop studied would be expected to influence the extent of lead absorption and this may partially explain the above lack of agreement among researchers using different plant species. The plant availability of lead was found to be inversely proportional to the exchange capacity of the soil (Miller et al., 1975a,b). Finally the form (Zimdahl et al., 1978) and rate of application (Baumhardt and Welch, 1972) of lead has been reported to affect the extent of absorption of lead by corn and other crops. Plant absorption was proportional to the rate of application of lead and the degree of water solubility of the particular salt used.

We did not observe a consistent soil pH-dependent absorption of lead by the plants. The concentration of lead in the soils was only increased by about 50 ppm as a result of incorporation of paper. The total concentration of soil lead in our study was far below those in many of the above referenced investigations, thus yielding only small differences in the lead content of the plants even when comparing the colored paper-grown crops with their respective controls. Owing to the number of factors beside pH which can affect lead absorption by plants, it is not surprising that a possible effect of soil pH may have been obscured.

In summary this study indicates that plants may absorb small amounts of lead if grown on soils which have been amended with colored magazine paper and newsprint. In normal agricultural practice the rate of application of paper to soil would have to be dictated by its rate of microbiological decomposition in order to avoid establishing an unfavorable carbon to nitrogen ratio for proper fertility and plant growth. The rate of application (10% by weight) used here probably represents an exaggerated level considering what might normally be incorporated in soil if paper is used as a mulching material. Realistically, however, one must take into account the possible accumulation of lead if smaller amounts of such paper were to be repeatedly incorporated in the same soil in succeeding years.

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^{13}C Nuclear Magnetic Resonance of the Amorphous Polymer of Lysine–Formaldehyde–Urea

Franklin E. Barton, II,* David S. Himmelsbach, and Henry E. Amos

The structure of an amorphous polymer of lysine–formaldehyde–urea was studied both as a solid and in solution with ^{13}C NMR. A peak at 44.6 ppm was assigned to the ϵ-carbon of lysine whose nitrogen was bound to a methylene or other substituent derived from formaldehyde. The ratios of bound and free lysine were determined for two different polymer preparations. The percentage free lysine in 2.5-day-old material was 65% for the polymer made with lysine monohydrochloride and 21% regardless of age when an equivalent amount of sodium hydroxide to neutralize the hydrochloride was added to the reaction mixture. Assignments of the chemical shifts were made by comparison with known literature values, model systems, and calculations of chemical shifts based on substituent parameters. Hydrolysis of the polymer in 1.0 N DCl under conditions similar to those of a ruminant abomasum yielded free lysine. ^{13}C NMR was shown to be a useful tool for the structural elucidation of the solid and that quantitative information can be obtained from the ^{13}C NMR spectrum of a solid.

Ruminant animals are unique among mammals because of the bacteria and protozoa in the ruminoreticulum which can utilize the energy from digested fibrous plant materials for synthesis of microbial protein. As such, ruminants can utilize energy from feedstuffs that man cannot digest. However, the quantity of microbial protein synthesized within the rumen may not be sufficient to meet ruminant requirements for growth and milk production (Hungate, 1965). Furthermore, microbial protein and many of the common protein supplements are deficient in one or more of three amino acids, i.e., methionine, lysine, and threonine. Nimrick et al. (1970a,b) found that for lambs microbial protein was deficient in these three amino acids. Also lysine and methionine were first and second limiting, respectively, or colimiting amino acids for dairy cows fed conventional diets (Schwab et al., 1976). Performance of growing cattle has been improved by abomasal infusions of a mixture of essential amino acids (Chalupa et al., 1973), lysine (Boila and Deulin, 1972; Deulin and Woods, 1964) and methionine (Steinacker et al., 1970; Fenderson and Bergen, 1975).

Supplementation of ruminant diets with free amino acids has not been practical because they are rapidly degraded by the rumen microorganisms (Broderick, 1975; Chalupa, 1976). Accordingly, several attempts have been made to protect amino acids from rumen degradation and have met with various degrees of success (Amos et al., 1974; Richardson et al., 1976; Langer et al., 1975).

This report describes the structure of a white amorphous polymer of lysine–formaldehyde–urea as determined by ^{13}C NMR. This polymer has been shown to protect about 55% of the lysine from rumen microbial attack, without affecting its biological availability (Amos and Evans, 1978a,b).

EXPERIMENTAL SECTION

Reagents. L-Lysine monohydrochloride, urea, and formalin (37% formaldehyde) were obtained as reagent

Field Crops Utilization and Marketing Research Laboratory, Richard B. Russell Agricultural Research Center, U.S. Department of Agriculture, Science and Education Administration, Athens, Georgia 30604.