

Mercury in Soil And Plant Systems: A Review of Literature

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No published data appear to be available concerning the mercury (Hg) content of soils in North Dakota. The most recent published data on soil Hg contents would appear to be of Swedish, Japanese and British origins (1, 3, 8, 21).

Andersson (3), using a neutron activation procedure, analyzed 273 Swedish and 14 African soils, and found the mean Hg contents to be 60.1 and 23 nanograms of Hg per gram (ng/g) of soil respectively. Cultivated soils generally contained more than did uncultivated soils, although both the maximum (922 ng/g) and the minimum (4 ng/g) contents were found in cultivated soil. The Hg tended to be concentrated in the surface soil; the surface soil contained five to ten times as much Hg as did the sub-soil. Retention of Hg in the surface soil appeared to be related to the contents of organic matter and clay minerals at low and high pH values respectively.

The Hg contents of some British soils were

found to vary between 0.25-1.00 to 5.00-15 ppm Hg, and were considered to be mostly of geological origin (21).

Aomine *et al.* (8) determined the Hg content of soils from seven paddy fields and five orange and three apple orchards, all of which with one exception had received 0.1 to 3 kg per hectare of Hg as mercurial fungicides in years preceding the investigation. Hg residues were confined to the surface layer in some soils, but in others an appreciable concentration of Hg occurred in the sub-soil.

The importance of soil composition on apparent Hg leaching was demonstrated by the finding that on one paddy soil which in the preceding 10 years had received approximately 1 kg per hectare of Hg only "trace" amounts (<100 ng/g) were found. The Hg determinations were made by a dithizone procedure.

Aomine and Inoue (7) studied the adsorption of phenyl mercuric acetate (PMA) and mercuric chloride by soil and clay minerals at Hg concentrations

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varying between 100 and 1,000 ppm. PMA was much more strongly adsorbed than the inorganic material. Phenyl mercuric ions or molecules were strongly held by clay minerals such as montmorillonite. In a subsequent paper, the same authors (11) added PMA labeled with ^{203}Hg at concentrations of 5×10^{-4} to 5×10^{-3} moles/liter. The pH of the clay was found to have a large influence on PMA adsorption, with the maximum adsorption occurring at pH 6 and with adsorption greatly reduced at pH 5 and 7. The high stability constant of PM hydroxide was considered to be the reason for the low adsorption at pH values greater than 7, and at low pH values competition with protons for adsorption sites was the stated apparent reason for the reduced adsorption.

The degradation of organomercury fungicides in a "sandy" soil was investigated by Kimura and Miller (12). Soil was treated with PMA and ethylmercury acetate (EMA) and methylmercury dicyandiamide and chloride (MMD and MMC). Metallic mercury vapor and trace amounts of PMA were present in the air surrounding PMA-treated soils. Most of the loss occurred from the surface inch of a soil column. About equal amounts of the vapor of metallic Hg and a volatile ethylmercury compound were present when EMA was used. With the use of methylmercury compounds, methylmercury vapor was present with trace amounts of mercury vapor. MMC was about twice as volatile as MMD when added to soil.

The organic mercurials were relatively persistent in the soils studied since a large portion of the applied compounds was still in the organomercury form after the lapse of 30 to 50 days. The tendency for mercury vapor to escape from soils was increased at low soil moisture contents. The authors were unable to substantiate the hypothesis of Boer (9) that dialkyl and diphenylmercury compounds were decomposition products of mercurial fungicides in soils. Boer (9) concluded that volatilization losses of mercury resulting from the addition of mercurial fungicides were insignificant.

The reason why mercury was slowly rendered ineffective by soil was considered to be due to the formation of mercuric sulfide. Ross and Stewart (16) postulated that the precipitation of mercuric sulfide would explain why residues of phenyl mercury acetate were confined almost entirely to the top two inches of soil. According to Lagerwerff (13) the only effective measure against contamination of soil with Hg seems to be the application of lime-sulfur or elemental sulfur, which apparently would

result in the precipitation of the very insoluble mercuric sulfide.

The presence of sulfide in soils is normally associated with strongly reducing conditions (6). However, since sulfate-reducing organisms are ubiquitous in nature (19) it is conceivable that within the environment of apparently "aerobic" soils, micro-anaerobic spots (in which sulfide could be produced) may occasionally be present. Also, during periods of temporary water-logging sulfides may accumulate in soil. Under aerobic conditions ferrous sulfide-S is very quickly converted to sulfate-S, but the more insoluble iron pyrites (FeS_2) may persist in soil for longer periods of time (10). Based on this finding, mercuric sulfide may be a possible end-product of mercury degradation in soils. However, Wiklander (22) concluded that mercuric sulfide formed in sewage sludge when exposed to air would be oxidized. The presence of mercuric sulfide in lake sediments would appear to be a distinct possibility.

Mercury pollution recently is under severe scrutiny in the United States because of the catastrophe which resulted from the Huckleby family of Alamogordo, New Mexico, eating mercury-contaminated pork during 1969 (15). Alkyl mercury is the form of mercury which is most poisonous, and which caused the mercury poisoning among members of the Huckleby family (5). Data from Japanese and Swedish researchers suggested that inorganic mercury could be converted into methyl mercury (a form of alkyl mercury) under natural conditions.

Wood *et al.* (23) subsequently showed that methylation of inorganic mercury could be accomplished by extracts of a methane-producing organism. Methane-producing organisms are widely-distributed anaerobic organisms, and because of their activity methylation of mercury might be occurring in lake sediments, sewage and anaerobic zones within soils. More research would appear to be needed concerning the extent and types of transformations involving mercury in sewage, soil, water and sediments.

The ability of soils to adsorb inorganic Hg is affected by organic matter contained in the water. Mekhonina (14) studied the adsorption of ^{203}Hg from lake water alone and from lake water extracts of leaves (pine, birch, aspen, and birdcherry) by three different types of soil by measuring the radioactivity of the solution before and after the addition of soil. Adsorption from the water alone was two to ten times greater than from the extracts. Adsorption from the extracts varied with species and the soil. The desorption of ^{203}Hg from soil by water

was greater when the water contained leaf extracts. Extracts of mosses and lichens also decreased adsorption.

Wiklander (22) recently reported on the content of Hg in Swedish ground and river water. The ground water samples were taken in the spring of 1968 from outlets of tile drainage systems in cultivated areas where no surface runoff water entered the systems. Concentration of Hg in the ground water was between 20-70 ng per liter. There appeared to be no relationship between the texture and/or origin of soil and the Hg content of the ground water. Water samples at three sites where Hg disinfection of seed had been regularly applied showed "average" contents of Hg. The Hg content of river water from upstream and downstream relative to the Uppsala, Sweden, mechanical and biological sewage treatment plant was essentially similar. According to the author this indicates that considerable amounts of Hg in the sewage water from domestic, commercial and industrial sources are retained by the sludge, probably as mercuric sulfide, deposited in the digestion tanks. The author quoted data by Andersson (2) showing that sewage sludge from eight different places contained 6,274 to 29,230 ng Hg per g of dry substance.

Wiklander (22) emphasized that Hg is found as a natural component in rocks, soils, water, the atmosphere and the biosphere and that circulation among these systems occurs. The industrial and agricultural use of elemental Hg and Hg compounds and the burning of fossil fuels, coal and petroleum, results in large amounts of Hg being transformed into water recipients, soils and the atmosphere. The same author appeared to accept Stock and Cucuel's finding (20) that rain water contained approximately 200 nanograms of Hg per liter; this value is appreciably above that found in the ground and river water samples and apparently indicates that soil and suspended particles adsorb much of the rain-transported Hg. Andersson and Wiklander (4) indicated that in Sweden about 1.2 g Hg per ha per year is brought into soil by rain water.

Literature concerning the uptake of Hg and the movement of Hg in plants has been reviewed by Smart (18). Trace amounts of Hg appear to be ubiquitous in plants. According to this author, the Hg content of ears of grain grown with mercury-treated seed was 0.01 ppm. More recently Saha et al. (17) found that although trace amounts of Hg were present in grain no significant difference in the mercury content of wheat and barley grains was found irrespective of whether they were grown from dressed grain.

Ross and Stewart (16) found that Hg applied as a spray to apples in the form of PMA moved in and from the foliage by translocation, not volatilization. The movement was principally to growing fruit and foliage. There was no apparent uptake of PMA through roots. Work at the Long Ashton Research Station quoted by Smart (18) indicates that appreciable amounts of Hg in nutrient solutions are taken up by plants and accumulate to the greatest extent in roots.

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