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RESIDUES OF MERCURY ON WHEAT TREATED WITH METALLIC MERCURY

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Treatment of wheat at 4 and 8 ppm of metallic mercury provided 87.5 and 90 percent respective control against four insect pest species tested i.e. *Tribolium castaneum, Trogoderma granarium, Sitophillus oryzae* and *Rhizopertha dominica*, over a storage period of 4 months. No significant difference in the insecticidal activity of mercury, applied either by mixing or placed in cloth packets was observed. Mercury residues on wheat treated at 4 and 8 ppm of mercury were detected to range from 0.25 to 0.29 ppm. The possible hazards involved in mercury treatment of foodgrains are discussed.

Key words: Residues, Mercury, Wheat, Storage, Village-level.

INTRODUCTION

At village level, about 70 percent of total grain production in the country is retained by farmers every year for self-consumption and seed purposes [4]. Due to lack of proper storage facilities in villages, grain is generally stored in mud built receptacles or piled in small stacks of gunny bags inside the living rooms [4, 18]. The storage losses, mainly due to insect pests [2], range from 2.5 to 5 percent with an even higher loss to the quality of stored grains [1-4]. Farmers often have to use labourious physical means like sun-drying, sifting and sieving to protect grain from insect damage, although these measures do not prove much effective. Since most of the convenient methods of disinfestation such as fumigation, are not easily practicable in village conditions [18], it is not surprising that quite a high proportion of farmers still use metallic mercury as grain protectant [4]. The practice of keeping metallic mercury in grain had been common in the villages of India and Pakistan since last century [5]. Generally, 5 to 10 grams of mercury, mixed with sand is distributed into layers of about one tonne of stored wheat, which is then sealed for subsequent storage in the mud-built receptacles.

The efficacy of metallic mercury against insect pests of stored grain has been demonstrated in various forms of application. This includes mercury-tin amalgums placed in grain [6], mercury placed in twill or long cloth bags and distributed throughout the bin [7], placing the strips of porous paper impregnated with mercury [8] and mercury mixed with chalk and applied to grains [5].

In view of the extreme toxicity of mercury compounds [10, 11, 19, 20, 22], which in the past have led to many fatal accidents in Iraq, Pakistan and Guatemala [9], its use in agriculture, mainly as seed-dressing, is restricted in many countries [10, 11]. The farmer's practice of using metallic mercury as grain protectant was therefore, needed to be studied for possible hazards involved. Present studies were carried out with a view to assess mercury residues on grain treated with metallic mercury. The results presented also deal with the efficacy of mercury in controlling the major insect pests of stored wheat.

MATERIALS AND METHODS

The mud bins used for the storage of wheat before and after treatment were oval shaped having an internal volume of 0.45 m^3 and wall thickness of 4.0 cm. These bins were comparatively smaller receptacles, built using clay and finely chopped wheat straw. A circular opening of about 45 cm in diameter was provided at top of each bin for loading and discharging of grain. The mud bins could be closed from top, using circular lids made of similar materials.

Insect free wheat with an average of 12.2 percent moisture content was divided into equal batches of 150 kg each. Five such batches were filled in separate mud bins and 200 numbers of freshly emerged, mixed sexes adults of each species of *Tribolium castaneum, Rhizopertha dominica, Sitophillus oryzae* and *Trogoderma granarium* were released and allowed to breed for 2 months. After that, the bins were opened and a representative sample of about 1 kg wheat was drawn from each batch. The base-line population of each insect species was recorded after sub-division of samples to 200 grams.

Pure mercury procured from local market was thoroughly mixed with wet sand in 1:700 ratio. Mercury-sand admixture was then mixed with two batches of previously infested wheat, at an application rate of 4 and 8 ppm of mercury. In another set of experiments, 6 x 6 cm cloth packets were filled with mercury-sand admixture and distributed in two batches of infested wheat in the mud-bins to provide a similar application of 4 and 8 ppm of mercury. A batch of untreated wheat, with known level of infestation was kept in a mud bin as control. The lids on the top opening of all the mud bins were sealed using mud-plaster. The bins were opened after a period of 4 months and insect population in representative samples was recorded.

For the analysis of mercury residues, samples were ground and 1 gram of each sample was digested in HC1. The volume of the solution after 24 hours digestion was made upto 100 ml. Blank samples were similarly prepared without using wheat. Blank and test samples were reacted with $KMnO_4$ to oxidise the insoluble compounds. The excess of permanganate was removed by reacting with hydroxylamine. Mercuric ions were extracted with chloroform solution of dithizone after adjusting pH to 1.5 [12]. Samples were then analysed in a mercury cold-vapour cell on an Atomic Absorption "Beckman-975 A" instrument.

RESULTS AND DISCUSSION

The results shown in Table 1 represent the average population of different insect species, recorded before and after the post-treatment storage of wheat over a period of 4 months. It will be seen that mercury treatment provided an effective control against all the insect species, at both the dose rates tested. An average of 87.5 to 90 percent reduction in the total insect population was recorded in wheat sample, treated with 4 and 8 ppm of mercury respectively when compared with untreated grain. The few surviving insects according to their decreasing numbers were *Trogoderma granarium, Tribilium castaneum, Sitophillus oryzae* and *Rhizopertha dominica*. The average number of both live and dead insects in treated wheat samples were, however, not significantly different from their respective numbers recorded before treatment. Whereas, in untreated wheat samples, an average number of 40 and 89 of live and dead insects was recorded against their respective pre-storage number of 5 and 40 insects over the same storage period. This showed that mercury treatment on grain also provided a control of the emergence of new insect progenies.

Application of mercury-sand admixture on wheat both mixed with grain or placed in cloth packets showed no significant difference in controlling the insect pests (Table 1). A reduction of 85 to 90 percent in the population of insects was recorded in wheat samples treated with 4 ppm of mercury, mixed with grain or placed in the cloth packets respectively. Similarly, application of 8 ppm of mercury, in either form on grain, showed a 90 percent control of total insect population.

The results of analysis of wheat samples for the residues of mercury after a post-treatment storage of 4 months are shown in Table 2. The level of residues at both the treatments was recorded to range from 0.25 to 0.29 ppm against 0.05 ppm in control. The level of mercury residues detected on wheat samples, treated either by mixing or placing mercury-sand admixture in cloth packets was also negligible.

The results (Table 1) showed that metallic mercury at both the application rates tested, effectively controlled the population build-up of insect pests in stored wheat, over a period of 4 months. The control of emergence of new progenies also confirmed earlier findings that metallic mercury has an ovicidal action on insects [5, 13, 14]. The eggs of insects were found to be destroyed on exposure to mercury vapours, while other stages were less affected [15].

Table 1. Average recover of introduced insect pests detected in a 200 gram sample of wheat before and after treatment with metallic mercury and its storage in mud bins for four months.

Dose of Mercury (ppm)	Form of application on wheat	Pre-treatment insect population												Post-treatment insect population											
		T. castaneum			*T. granarium*			*R. dominica*			*S. oryzae*			*T. castaneum*			*T. granarium*			*R. dominica*			*S. oryzae*		
		A	L	P	A	L	P	A	L	P	A	L	P	A	L	P	A	L	P	A	L	P	A	L	P
4.0	Mixed with grain	*3.0	–	–	2.0	–	–	–	–	–	–	–	–	1.0	–	–	4.0	–	–	–	–	–	1.0	–	–
		**7.0	1.0	–	15.0	4.0	–	14.0	–	–	1.0	–	–	9.0	–	–	27.0	6.0	–	12.0	–	–	2.0	–	–
8.0	Mixed with grain	*5.0	–	–	–	–	–	–	–	–	–	–	–	4.0	–	–	–	–	–	–	–	–	–	–	–
		**6.0	1.0	–	13.0	8.0	–	7.0	–	–	1.0	–	–	8.0	–	–	20.0	4.0	–	8.0	–	–	3.0	–	–
4.0	Placed in cloth packets	*–	–	–	4.0	–	–	–	–	–	1.0	–	–	2.0	–	–	2.0	–	–	–	–	–	–	–	–
		**2.0	3.0	–	29.0	6.0	–	7.0	–	–	5.0	–	–	3.0	1.0	–	19.0	8.0	–	5.0	–	–	2.0	–	–
8.0	Placed in cloth packets	*–	–	–	2.0	–	–	1.0	–	–	1.0	–	–	1.0	–	–	2.0	–	–	–	–	–	1.0	–	–
		**6.0	–	–	12.0	1.0	–	4.0	–	–	3.0	–	–	12.0	–	–	16.0	2.0	–	3.0	–	–	2.0	–	–
Control	—	*1.0	3.0	–	1.0	–	–	–	–	–	–	–	–	7.0	3.0	–	3.0	–	–	10.0	14.0	–	3.0	–	–
		**8.0	3.0	–	8.0	–	–	16.0	–	–	5.0	–	–	28.0	1.0	–	37.0	1.0	–	14.0	–	–	8.0	–	–

* = Alive, ** = Dead, A = Adult, L = Larva, P = Pupa

Metallic mercury is volatile, having a vapour pressure of 1.2 x 10^{-3} mm at 20° [16] and its insecticidal action is attributed to its vapour phase [5, 15, 17, 29]. The insignificant difference observed in the efficacy of metallic mercury, in either form of application tested (Table 1), also confirms these findings. Moreover, equivalent levels of mercury residues detected at both the application rates tested (Table 2), indicate possibly the saturation of surrounding air with mercury vapours at similar temperatures.

Table 2. Residue of mercury detected on wheat treated with metallic mercury after 4 months post-treatment storage.

Application rate of mercury (ppm)	Form of application on wheat	Residues of mercury (ppm)
4.0	Mixed with grain	0.2644
8.0	Mixed with grain	0.2770
4.0	Placed in cloth packets	0.2512
8.0	Placed in cloth packets	0.2910
Control	—	0.0566.

Mercury vapours being 6.68 times heavier than air have a limited penetration range of about 1 meter through the bulk grain [5]. The use of mercury as grain protectant, thus, in contrast to fumigants, do not require a high standard of gastightness of the receptacles. It is therefore, a convenient and effective method of insect pest control, traditionally used by the farmers for safe storage of grain in mud-built granaries, generally not suitable for fumigation [18].

In contrast to its organic and inorganic compounds, metallic mercury, when taken orally, is found to be relatively less toxic to man [11]. Toxic signs were rarely observed in patients, who received oral doses of 100 to 500 grams of mercury in the treatment of bowel obstruction [19]. In comparison to this, average daily intake of persons poisoned by seeds treated with organo-mercury compounds was found to be 2.7 mg per person per day [10]. Bornmann *et al* [25] observed 10 fold increase in the concentration of mercury in blood and kidneys of rats, oraly administered with metallic mercury. However, the extent of absorption appeared to be relatively low and dangers of poisoning from metallic mercury by this route seemed slight [26]. It is due to the fact that elemental mercury must undergo oxidation to mercurous or mercuric form, to react with proteins and other molecules in living systems. The inhalation of mercury vapour on the other hand, is very injurious to lungs and in acute cases may affect central nervous system [20]. Stock *et al* [21] showed that metallic mercury in aqueous solutions, is rapidly oxidised in the presence of air. Moreover, virtually complete absorption of mercury vapour through lungs and its oxidation in red blood cells and other tissues [22] explains the highly hazardous nature of mercury vapours.

The toxicity of mercury and its compounds has extensively been reviewed [11, 19, 22, 26]. Ingestion of 30 μg of methyl mercury was considered as the highest safe level [23]. The Joint FAO/WHO Experts Committee on Food Additives in their sixteenth report [24], recommended a provisional tolerable weekly intake of 0.3 mg of total mercury, of which not more than 0.2 mg should be in the form of methyl mercury (expressed as mercury). Considering the average intake of wheat which forms major part of our daily food, the levels of mercury residues detected on treated wheat (0.25 to 0.29 ppm, Table 2), were quite higher than the safe limits. The residues of mercury in untreated samples of wheat (0.05 ppm) appeared to be the instrumental error. Moreover, the levels of mercury residues were not lowered after sun-drying or washing of the treated wheat samples (not shown in Table 2). It appears, therefore, that mercury vapours after absorption on grain are converted into some form of non-volatile, fixed residues, possibly due to its oxidation. Earlier studies [27, 28] also indicate the same fact, where treatment of grain with saturated mercury vapours for 20 days was found to be ineffective against insect eggs, subsequently laid on grain. The consumption of foodgrains containing hazardous residues of mercury may not show symptoms of acute poisoning, but its long term accumulation in the body [22] can lead to various ailments. Therefore, the traditional practice of applying mercury on foodgrains in villages needs to be replaced with safer and effective methods for the safe storage of grain.

REFERENCES

1. H. Ahmed, Losses Incurred in Stored Foodgrains by Insect Pests, (published by Pakistan Agricultural Research Council, Islamabad, 1984),p. 14.
2. H. Ahmed, M. Ahmed and A. Ahmed, Protection of stored bagged stored by government agencies in Pakistan - A scrutiny of current practices and recommendations for improvement, Rep. No. 3, Grain Storage Research Laboratory, PARC, Karachi-32, (1987).
3. Anonymous, A study of problems associated with procurement, storage and distribution of wheat, MICAS Associates (Pakistan) Ltd., Karachi (1976).
4. C.P.F. De Lima and M.N. Saqib, Survey of farm-level storage losses in wheat in 1984-85 storage season,

PFL/PAK 002, Field Document No.5, FAO, Islamabad (1985).
5. M.M. Nasir, Bull. Ent. Res., 40(2), 299 (1949).
6. G.R. Dutt and A.N. Puri, A simple method of storing food Agri. J. India, **24**, 245 (1929).
7. K.A. Rahman, Indian J. Agri. Sci., **12**, 564 (1942).
8. K.K. Dole, Observations on the insecticidal properties of mercury and its economical use for preservation of damage to stored food grain, Univ. Bombay, (N.S.), 11(A):116-120 (1943).
9. L.J. Goldwater, Scient, Amer.. **15**, 224 (1971).
10. Anonymous, The use of mercury and alternative compounds as seed dressings, Report of joint FAO/WHO meeting, FAO Agric. Studies No. 95, FAO Rome (1974).
11. J.G. Saha, Significance of mercury in the environment, Residue Reviews, 42, 103 (1972).
12. Anonymous, Determination of mercury content of foodstuffs, International Union of Pure and Applied Chemistry, Pure App. Chem. **10**, 77 (1965).
13. K.K. Kannan, Mercury as an insecticide, Proc. 3rd Ent. Mtg. Pusa, held in 1919, 761-762 (1920).
14. A.O. Larson, J. Econ. Ent., **15**, 391 (1922).
15. H.C. Gough, Nature, **141**, 922 (1938).
16. R.C. Weast (Ed), Handbook of Chemistry and Physics, 64th Edition (CRC press, Inc. Florida, 1984.
17. B. Krishnamurti and S.M. appanna, Curr. Sci., **14**, (1945).
18. M.Q. Chaudhry and M. Anwar, Pakistan J. Sci. Ind. Res., 31, 126 (1988).
19. P.L. Bidstrup, Toxicity of mercury and its compounds, Elsevier, Amsterdam (1964).
20. C.T. Teng and .C. Brennan, Acute mercury vapour poisoning: A report of four cases with radiographic and pathological correlation, Radiology, **73**, 354 (1959).
21. A. Stock, F. Cucuel, F. Gerstuer, H. Kohle and H. Lux, Z. Anorg. Chem., 217 (1934).
22. T.W. Clarkson, Ann. Rev. Pharmacol., **12**, 375 (1972).
23. P.M. Newberne, Fd. Technol., **4**, 311 (1974).
24. FAO/WHO Joint Committee on Food Additives: Evaluation of mercury, lead, cadmium and the food additives amaranth, diethyl pyrocarbonate and octagallate, WHO Food Additive Ser., **4**, 1 (1972).
25. G. Bornmann, G. Henke, H. Alfes and H. Mollmann, Uber die enterale resorption von metallischem quecksilber, Ach. Toxicol., **26**, 203 (1970).
26. R.l. Bradley and A.g. Hugunin, Mercury in Food, Feed Stuffs and the Environment, In: The Safety of foods, IInd ed. (AVI, Publ. Co. Inc. West Port Connecticut, 1980) IInd ed.
27. O.W. Richards, Bull. Ent. Res., **36**, 283 (1945).
28. R.E. Blackith and B.S. Gorringe. Bull. Ent. Res., 44(2), 217 (1953).