A GC/MS Investigation of Organic Chemical Residues Found in Agricultural Soils

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INTRODUCTION

The treatment of seed potatoes with mercurial solutions, to control a wide range of latent diseases and rots, has been carried out in Scotland for more than twenty years. This paper reports an investigation into the operation of one such potato treatment plant and the disposal of its effluent. The organomercury compound used in the treatment process was methoxyethylmercuric chloride under the trade name 'Agallol' (a 2.5% concentration manufactured by Farbenfabriken Bayer A G, West Germany). The study was undertaken after high levels of mercury were found in aquatic vegetation in the stream receiving the waste liquors from the treatment process.

The dipping of the potatoes was carried out during a period of approximately ten weeks in the autumn. Prior to treatment, potatoes were washed to remove soil adhering to the skins and were then immersed in a 1000 gallon (4500 l) bath of methoxyethylmercuric chloride at a concentration of 120 ppm mercury. The organomercury solution was renewed every three or four days, when the concentration of mercury had fallen to approximately 80 ppm. The discarded solution was pumped to two storage tanks and was treated with sodium sulphide with the intention of precipitating mercuric sulphide. After twentyfour hours of forced circulation, without settlement, the liquor was pumped to a soakaway pit from which the water drained through a sand bed into the ground.

The potato wash water was passed through two settling tanks before discharge to an underground drainage system connected to a culvert with an outfall to an adjacent stream, the Commerton Burn. (Figure 1). This rather silty, slow-flowing stream enters a small river, the Dean Water, at a distance of about 800 metres below the culvert outfall. This river contains brown trout (Salmo trutta L.) and grayling (Thymallus thymallus) which are taken and eaten by anglers.

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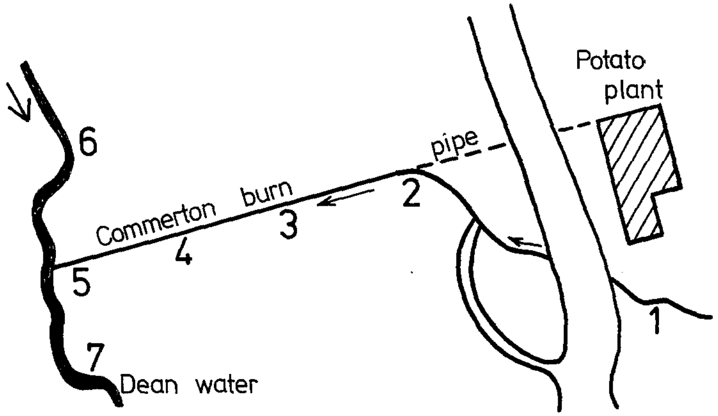

Figure 1. Sampling Sites.

The streams form part of the River Tay catchment, which is under the jurisdiction of the Tay River Purification Board, and samples taken by the Board in 1971 from the culvert outfall were found to contain mercury. At the end of 1971 a plant sample taken from the Commerton Burn below the culvert discharge point was submitted by the Inspector of the Board to the University of Dundee for mercury analysis, and high levels of mercury were found in leaf, stem and root. The Board subsequently asked the Pitlochry laboratory to investigate the extent of the pollution.

SAMPLING AND ANALYTICAL METHODS

Plant specimens were obtained by hand collection and sediment samples by means of a hand-operated scoop fitted with a nylon mesh filter to enable surplus water to drain off. Fish were sampled by electro-fishing. Plant material was washed and both plant and sediment samples were dried at not more than 40°C in a drying cabinet on return to the laboratory. Fish tissues were dissected and deep-frozen until required for analysis. Total mercury was determined by wet oxidation with a mixture of nitric and sulphuric acids (4:1) followed by cold vapour atomic absorption spectrophotometry. (HOLDEN 1973).

1972 SURVEY AND RESULTS

The first survey of the Commerton Burn was made in August 1972 before treatment operations had begun. Plant and sediment samples were collected from sites along the Commerton Burn and sampling was continued at intervals during and after the operation of the potato plant. Fish samples were obtained when possible from the Commerton Burn and the Dean Water.

The results of the total mercury analyses of the sediments are shown graphically in Figure 2.

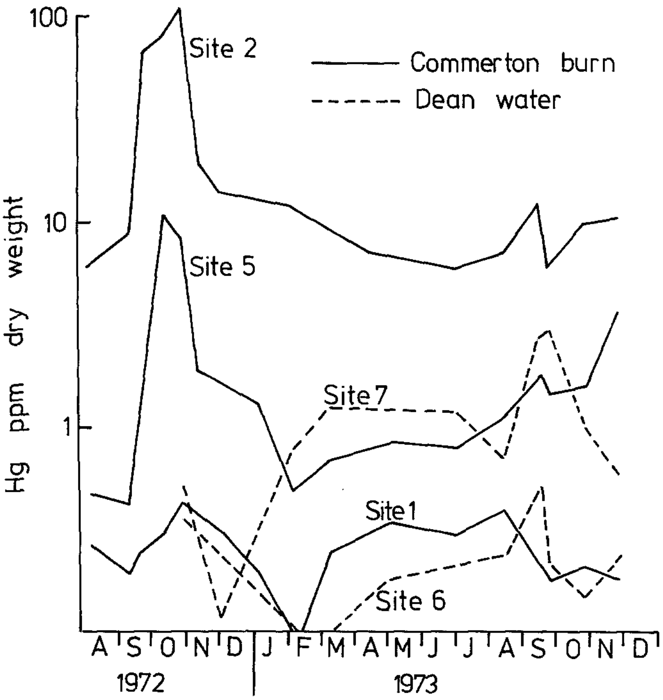

Figure 2. Mercury concentrations in the sediments.

In August, the sediment from the culvert outfall point (Site 2) contained almost 6 ppm mercury. At Site 1, above the potato treatment plant, the mercury content was 0.26 ppm and at Site 5, 800 metres below the culvert outfall, the sediment level was 0.46 ppm. Mercury treatment began in September and it can be seen that there was a very significant increase in the mercury level of the sediment to 100 ppm at Site 2 by the end of October. At Site 5, the level had risen to more than 10 ppm, whereas above the culvert outfall (Site 1) the concentration was 0.39 ppm. During November the treatment stopped, and sediment mercury at Site 2 decreased rapidly to less than 14 ppm by December, while at Site 5 it fell to less than 2 ppm.

Similar trends were reflected in the mercury content of the vegetation. The submerged macrophyte, Callitriche sp., showed a dramatic increase in mercury from 1 ppm to 2215 ppm dry weight at Site 2 in October and to more than 700 ppm at Site 5.

TABLE 1

Total mercury in Callitriche species (ppm dry weight)

Date	Commerton Burn				Dean Water	
	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
9. 8.72	1.6	-	1.0	-	-	-
13. 9.72	1.1	-	-	0.8	-	-
19.10.72	2215	628	581	737	-	-
31.10.72	1718	118	390	434	1.0	-
21.11.72	-	229	-	259	-	-
6. 9.73	-	-	0.8	-	-	0.6
1.10.73	-	1.3	-	-	-	0.5
1.11.73	-	2.2	-	1.2	0.2	-

The emergent species, Myosotis sp., attained values of almost 300 ppm, compared with less than 1 ppm in August.

TABLE 2

Total mercury in Myosotis species (ppm dry weight)

Date	Commerton Burn					Dean Water	
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
9. 8.72	0.5	-	0.6	0.4	0.4	-	-
13. 9.72	0.7	-	-	-	-	-	-
31.10.72	-	217	176	208	294	0.8	34.5
14. 2.73	-	8.2	0.7	1.9	24.5	-	-
21. 3.75	-	30.3	6.6	2.0	2.4	-	-
8. 5.73	-	-	1.6	2.3	-	-	-
12. 7.73	-	-	-	0.2	0.3	-	-
15. 8.73	-	1.3	0.3	0.3	0.2	-	-
18. 9.73	-	2.8	0.3	0.6	0.3	0.3	0.1
3.10.73	-	0.9	0.2	0.2	0.1	0.2	0.2
1.11.73	0.1	0.8	0.3	0.2	0.2	0.1	0.1
5.12.73	-	2.0	0.2	0.3	0.2	0.1	0.1

Mean mercury concentrations in fresh muscle tissue from brown trout and grayling are given in Figure 3. Mean values of 8-9 ppm were found in both species in the Commerton Burn in October, but levels fell off rapidly on cessation of the mercurial treatment, to less than 1 ppm. Some fish in the Dean Water contained more than 2 ppm mercury during October and November but the mean level had dropped to less than 0.5 ppm by December.

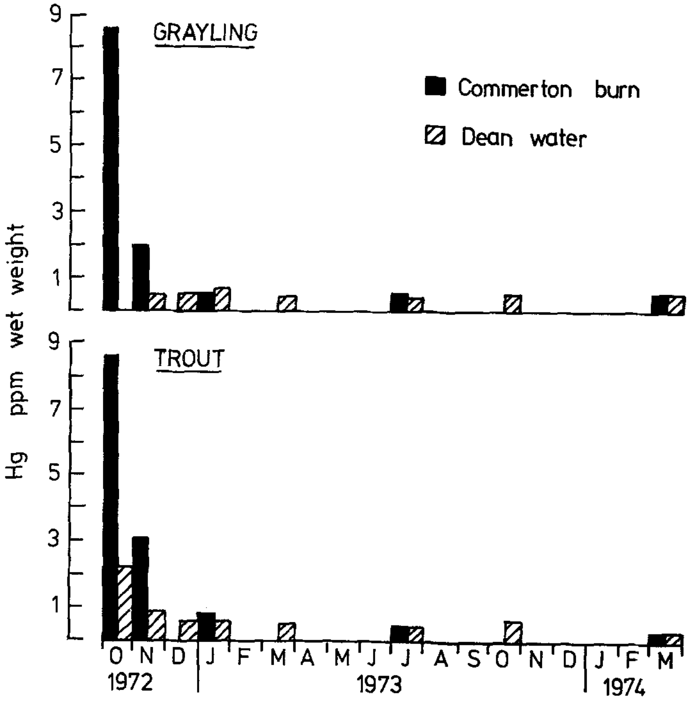

Figure 3. Mean Hg concentrations in fish muscle.

INVESTIGATION OF THE DETOXIFICATION PROCESS

The results of the 1972 survey suggested that there was a leakage of mercury from the soakaway at the treatment plant into the field drain and culvert which discharged into the Commerton Burn. An analysis of the supernatant liquor from the precipitation tank gave a total mercury concentration of 46 ppm. Silt, filtered from the culvert effluent, contained 50 ppm mercury. The detoxification process involved an inefficient method of treating the spent liquor from the dressing plant, as much of the methoxyethyl mercury in the liquor remained in solution and was stable at the pH of the liquor (pH 8). It seemed likely that the liquor, after discharge to the soakaway bed, had percolated through to a field drain, or had otherwise entered the culvert conveying the potato wash water, and resulted in a discharge of methoxyethyl mercury to the Commerton Burn. A high concentration of this chemical was retained in the sediment in the stream.

The original concentration of mercury in the dipping baths was 120 ppm and the liquor was discarded as 'spent' when the concentration fell to 80 ppm. At the end of 1972, samples of spent liquor were treated with 0.14% $^{w}/v$ sodium sulphide but no obvious settlement of mercury as sulphide occurred within 24 hours. Attempts to destroy the methoxyethyl mercury by converting it to the inorganic form with strong acid prior to sulphide treatment were not effective above pH 1.3, and even at this pH the reaction was slow. In view of the time taken, the amount of acid required (3 gallons concentrated sulphuric acid for 1000 gallons of liquor) and the disposal problems of such liquids, this method was not further investigated. A number of flocculating agents were tested in the laboratory, including ferrous sulphate, ferric sulphate, aluminium sulphate and Polyflok 13 CL. Samples of spent liquor were treated with both 0.14% $^{w}/v$ sodium sulphide and one of the flocculating agents, and the precipitates allowed to settle overnight. The only effective one was 0.2% $^{w}/v$ ferrous sulphate. The precipitate of ferrous carbonate or bicarbonate settled rapidly, carrying down all but about 1 ppm mercury. Four batches of spent liquor, each of about 1000 gallons, treated with sodium sulphide followed by ferrous sulphate and allowed to settle overnight, gave mercury concentrations of 0.8, 0.8, 0.8 and 2.0 ppm in the supernatant. In the absence of the sodium sulphide, settling of the mercury was much less effective. Laboratory tests indicated that the ferrous sulphate should be added at not less than 0.2% $^{w}/v$. In August, 1973 the plant operators were advised to adopt the sodium sulphide - ferrous sulphate treatment, allowing the sludge to settle overnight before spraying the clear supernatant liquor on waste land reserved for the purpose. This method of disposal was calculated to have doubled the mercury content of the upper 20 cm of soil over an area of 0.1 ha, and could not therefore be repeated indefinitely at the same site, unless this was assigned to mercury disposal, and not subsequently used for agricultural purposes.

1973 SURVEY AND RESULTS

Sampling of sediment, vegetation and fish from the Commerton Burn and Dean Water was continued in 1973. Treatment of the potatoes began on 24 September and ended on 14 November. Figure 2 shows that the mercury in the sediment at Site 2 remained at 5-10 ppm throughout the treatment programme. Levels of 2-3 ppm mercury were observed at Sites 3, 4 and 5 but these probably resulted from movement of silt from Site 2. There was no significant increase in the mercury content of the *Callitriche* and *Myosotis* samples (Tables 1 and 2).

Total mercury analyses of fish muscle are summarised in Tables 3 and 4.

TABLE 3

Total Mercury in Trout Muscle (ppm wet weight)

	Commerton Burn			Dean Water above Commerton Burn			Dean Water below Commerton Burn		
	1972	1973	1974	1972	1973	1974	1972	1973	1974
Number of Fish	24	22	13	2	32	8	22	43	6
Weight Range g	8 - 1028	43 - 493	9 - 234	59 - 98	20 - 508	31 - 470	35 - 215	16 - 439	26 - 154
Hg Range ppm	0.1- 19.8	0.1- 4.7	0.1- 0.4	0.1- 0.6	0.1- 0.6	0.1- 0.3	0.1- 5.8	0.1- 0.8	0.1- 0.2
Mean Hg ppm	5.7	0.6	0.2	0.4	0.2	0.2	0.8	0.3	0.2

TABLE 4

Total Mercury in Grayling Muscle (ppm wet weight)

	Commerton Burn			Dean Water above Commerton Burn			Dean Water below Commerton Burn		
	1972	1973	1974	1972	1973	1974	1972	1973	1974
Number of Fish	11	16	4	32	19	9	39	24	6
Weight Range g	12 - 27	16 - 449	12 - 158	103 - 439	103 - 484	80 - 330	22 - 496	17 - 612	21 - 307
Hg Range ppm	0.2- 11.8	0.2- 0.6	0.2- 0.4	0.1- 0.3	0.1- 0.2	0.2- 0.4	0.1- 0.9	0.1- 1.0	0.1- 0.3
Mean Hg ppm	5.2	0.4	0.3	0.2	0.2	0.3	0.3	0.4	0.2

The mean level in trout muscle in Commerton Burn fish in 1973 was 0.6 ppm Hg. This shows a significant reduction in mercury concentration compared with 5.7 ppm Hg in 1972. A similar striking decrease occurred in grayling muscle. The mean concentration fell from 5.2 ppm in 1972 to 0.4 ppm in 1973. Also, the concentration range in samples of both trout and grayling in 1973 was much smaller than in 1972. In trout, apart from one fish with 4.7 ppm Hg, the range was 0.1 - 1.1 ppm whilst in grayling it was 0.3 - 0.7 ppm.

Mercury concentrations in Dean Water fish, below the Commerton Burn junction, did not decrease quite as dramatically as those nearer the polluting source but the maximum found for trout fell from

5.8 ppm in 1972 to 0.8 ppm in 1973 and the mean value decreased by more than 50%.

A single eel caught in the Dean Water downstream of the Commerton Burn in 1972 contained 5.8 ppm Hg and one from the same burn in 1973 contained 15.4 ppm Hg in the muscle tissue. The mean mercury level in sixteen eels from the Dean Water upstream of the Commerton Burn in 1973 was 0.3 ppm (range 0.1 - 0.8 ppm), and in twenty eels downstream of the Commerton Burn was 1.8 ppm (range 0.5 - 3.6 ppm). As eels usually feed on or near the bottom of streams, these high mercury levels are probably associated with feeding habit and intake, during feeding, of contaminated sediment.

DISCUSSION

In general, trout and grayling caught in areas with no obvious contaminating source have concentrations of mercury in the muscle tissue of less than 0.10 ppm wet weight. If the levels are greater than 0.20 ppm it may be inferred that the fish have been exposed to an elevated level of mercury. A total of 167 samples of brown trout from locations throughout Scotland gave a mean mercury concentration of 0.09 ppm and 39 grayling from eight Scottish rivers had a mean concentration in the muscle tissue of 0.07 ppm. Values of 0.05 ppm (RUCKER 1968) and 0.09 ppm (JOHNELS et al 1967) have been reported as normal for freshwater fish. In the present study, total mercury concentrations up to 20 ppm and 12 ppm in brown trout and grayling respectively were recorded. These levels were indicative of a polluting source.

During attempts to trace this pollution it was found that the 'detoxified' spent liquor from the treatment plant contained more than 40 ppm mercury. GRIMSTONE (1972) states that a large proportion of mercury lost in effluent is retained by sediments and subsequently released over a period of years. Sediment levels in the St. Clair river near the Dow Chemical sewage outfalls reached concentrations as high as 1700 ppm (ONTARIO WATER RESOURCES COMMISSION 1970). High levels have also been recorded below paper mills and chlor-alkali plants in Sweden and in river muds near Japanese industrial plants (HOLDEN 1972). In this investigation, stream sediment at the culvert outfall point gave a maximum concentration of 100 ppm dry weight. Macrophytes rooted in the contaminated sediment also exhibited very high levels of mercury contamination. The revised treatment recommended to the plant operators and adopted by them for the 1973 treatment programme produced significant reductions in the total mercury residue levels in fish muscle, sediments and aquatic plants.

As the larger trout and grayling (above about 100 g) in the Dean Water are taken by anglers and subsequently eaten, the mercury concentrations in the fish are of some concern, the generally accepted limit for fish used as food being 0.5 ppm. The highest concentrations were found mainly in juvenile fish near the source of contamination but in 1972 a significant proportion of fish taken by anglers contained more than 0.5 ppm. Following the adoption of the revised waste treatment process in 1973, few exceeded this level and in 1974 no trout or grayling were found with more than 0.4 ppm. The mean values, however, were still significantly above the levels normally expected for the species.

All the analytical data obtained were in terms of total mercury. A few of the fish analysed in 1972 were found to have 5-63% of mercury in the methyl form but in other fish of the same species from unpolluted areas more than 90% of mercury was in the methyl form. It could not be established whether the remaining mercury in the contaminated fish was inorganic or in the methoxyethyl form, as the extraction procedure used for methyl mercury prior to GLC analysis destroyed the methoxyethyl compound. This form is regarded as of lower toxicity than methyl mercury, and is relatively easily metabolised to inorganic mercury.

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