International Council for the
Exploration of the Sea

C.M.1971/E:6
Fisheries Improvement Committee

Investigations on Traces of Mercury Compounds in Fish and Fish Products

by

J. Wierzchowski[x)]

Introduction

One of the most striking changes in public health after the last world war has been an enormous increase in the incidence of food poisoning. Food may be inherently poisonous, or poisons may find their way into it. Poisoning from inherently poisonous food is rare. Much more food poisoning is nowadays due to contamination of food with chemicals.

In the present usage, pesticides are those chemicals successfully and commercially used for combating the pests that interfere with the production, transport and storage of agricultural crops and products. There are lots of these chemical compounds.

The group of mercury-containing compounds has been employed to a large extent in treatment of some cereals and vegetable seeds as well as flower bulbs. These chemicals are also widely used in soil treatment in control of turf diseases. Mercury is used in the form of dilute solutions of mercuric chloride or more commonly, of organic mercury compounds such as phenyl mercuric acetate and methoxyethyl mercuric chloride. According to Mc Callan et al.(1), there are approximately twenty-five organic mercury compounds that may be used as fungicides.

Mercurial fungicides have been the target for considerable criticism in some countries, especially in recent years in Japan and Sweden. Opponents have stressed great human health hazards in their preparation, application and as chemical residues in food. All mercurials are toxic to some degree and this property possibly depends on their capacity for combining with and immobilising sulfhydryl groups which are so important in many enzyme reactions (2).

The hazardous nature of mercury residues in foodstuffs was emphasised in the 1950's at Minamata, Japan, where severe neurological disorders among people living in the area were recorded, mostly ending with severe disability or fatally. Investigations have shown that effluent containing mercuric chloride from a nearby factory had been discharged into the bay, causing contamination of water and sludge, and that fish caught from the bay contained significant amounts of mercury. All the persons affected had eaten fish or shellfish which contained high levels of mercury caught in the Minamata Bay. A methylmercury compound in the fish was considered to be the main toxic agent (3).

x) Department of Bromatology,
Medical Academy
Gdánsk, Poland

Ground water containing dissolved matter reaches the sea by way of rivers, or directly by seepage along the shore. This is the main source of dissolved matter and various components accumulating in rivers and near-shore sea waters. Along the coast the sea receives used water polluted with sewage, domestic and industrial effluents, mostly without any previous cleansing treatment, either directly or via river mouths. Far away from the shore the sea water may not be so heavily polluted, but faecal and industrial pollution of the marine environment is almost a coastal phenomenon.

All that was said above indicates that fish - marine fish and freshwater fish - justly considered one of the wholesome and sanitary foods at the time they are caught, no longer possess this high degree of wholesomeness.

Foodstuffs normally contain traces of mercury, the amount depending on the environment in which they are grown or bred and on any external application of mercury-containing compounds. Fish tend to accumulate mercury and can have higher levels than other products. Accumulation of mercury in fish has been particularly noticeable in rivers and lakes in Sweden, as well as in some near-shore Baltic sea water as a result of mercurial effluent, arising from use in agriculture and in drainage from paper mills. (4,5,6,7,8).

In this connection, there have appeared problems of fish contamination and even fish life destruction. Water pollution is becoming a real hazard not only to animals but also to human health.

The intention of the present paper is to give information about investigations on mercury compounds in fish and some fish products, conducted in the Department of Bromatology , Medical Academy in Gdánsk during the last two years, i.e. 1969 - 1970.

Experiments

The following fish and fish products were examined in the present investigation :

a) Marine fish - cod (Gadus norhua), herring (Clupea harengus) and some canned products prepared from these fish, altogether 66 samples.

b) Freshwater fish - tench (Tinca vulgaris), bream (Abramis brama) perchpike (Lucioperca sandra), whitefish (Coregonus spp), zahnte (Vimba vimba)and some canned products prepared from these fish - altogether 51 samples.

A number of methods for the estination of mercury in food have been described. Smart (3) has divided all methods for mercury residue analysis into four groups. In general, the analysis of these compounds depends on the destruction of organic matter, isolation of the mercury and estination of the isolated mercury.

In our Department mercury was determined by the wet oxidation method reported by Hordyńska et al.(9, 10) and Legatowa et al.(11) modified in some details for fish and canned fish products. Like the authors mentioned, the Gorsuch-Onrust apparatus for mineralisation of the samples with nitric-sulphuric-perchloric acids was applied, using dithizone extraction for measurement of the mercury. It was found that the method can be applied when the content of mercury in the analysed sample is higher than 2 µg. The limit of detectability of the method required the samples to be fortified. For this purpose, a "summary extraction" was applied, using the same dithizone to extract mercury

from two or three mineralised samples of fish or canned fish products. An exact description of the method adapted in our investigations and detailed results of the analysis will be published by Wierzchowski and Nabrzyski (12) in the periodical "Bromatologia i Chemia Toksykologiczna". The present paper gives only preliminary information about contamination of fish and fish products by mercury in our country as well as a short general discussion of the subject.

Results and discussion

The fact that mercury pesticides are toxic is amply illustrated by the histories of accidental poisoning published in daily papers and in professional literature. The problem raised by the presence of mercury residues in food has caused considerable anxiety among public health authorities. There are many aspects of this problem of mercury residues in foodstuffs where the first need is for quantitative and analytical data in order to be able to assess the hazard at a stage before the question of the potential toxicity arises at all.

Freshness and decomposition of fish are recognised by several well defined signs, but it is difficult to recognise the presence of such poisonous substances as mercury compounds. Fish, which to all appearances are healthy, are sometimes responsible for symptoms of poisoning in man. Some of these poisonings may be the result of poisonous substances present in the water where the fish live. Certain observations indicating the presence of mercury in fish and canned fish products (2,3,5) led us to undertake this investigation with Polish caught fish and canned products made from these fish.

The interesting point of the results of the analysis of marine fish (cod and herring) and of canned products prepared from these fish is that no mercury was found in the analysed samples, but in a few cases recovery of mercury in fortified samples amounted to 110 - 120% Hg. Similar results were found in a few samples of fish (bream) caught in the mouth of the river Wisla. It shows that traces of mercury are present in investigated samples of fish and fish products - traces which could not be determined by the adapted method.

The results obtained with fish from the coastal area - from Wdzydzkie lakes - and with some canned products from these fish gave a slightly different picture, because it was found that some samples contained between 0 and 7.7µg of mercury in 100 g of sample:

Tench (5 samples)	2.5 to 4.0 µg Hg/100g
Perchpike (3 samples)	6.3 to 6.8 µg Hg/100g
Whitefish (3 samples)	0 to 2.8 µg Hg/100g
Zahnte (2 samples)	2.8µg Hg/100g
Zahnte in oil (2 samples)	7.7µg Hg/100g

According to Lundholm (13) the mean levels in fish from two Swedish lakes ranged from 30 to 80µg compared with corresponding values of 7µg and 10µg Hg/100g in Norway and Switzerland respectively. Smart (3) has given figures for the mercury content of some marine fish eaten in Sweden as between 1.6µg and 11µg Hg/100g and of some freshwater fish as between 1.0µg and 395µg Hg/100g

Conclusions

On the basis of the literature and the investigations described above, the following conclusions were reached :

The results of the analysis call attention to the need for determination of mercury residues in fish and fish products.

It appears important to direct the research not only towards estimation of mercury compounds in fish and fish products, but also towards tracing their origin and eliminating pollution of the waters. The situation seems to require careful watch if the use of mercurial pesticides continues to increase.

It is obvious that much remains to be learned about marine and freshwater fish contamination and poisoning with mercury compounds in our country.

References

1. MC CALLAN, S.E.A., MILLER, L.P. and MAGILL, M.A., 1955. Phytopathology, 45:295.

2. BIDSTRUP, L.P., 1964. Toxicity of mercury and its compounds. Elsevier Publishing Company. Amsterdam-London-New York.

3. SMART, N.A., 1968. Residue reviews. Ed. F.A. Gunther, Springer Verlag Berlin-Heidelberg-New York.

4. WESTOO, G., 1967. Vår Föda,19:1.

5. WESTOO, G., 1968. Acta Chem. Scand., 22:2277.

6. WESTOO, G., 1966. Ibid, 20:2131.

7. WESTOO, G., 1967. Ibid, 21:1790.

8. FALK, R., SNISH, J.O., EKMAN, J., GREITZ, U., Åberg, B., 1970. Acta Radiologica 9:55.

9. HORDYNSKA, S., LEGATOWA, B., BERNSTEIN, I., 1962. Chemia Analityczna, 7:567.

10. HORDYNSKA, S., LEGATOWA, B., KOBYLECKA, K., ROZYCKA, D., STRYCHARSKA, M., ROCZNIKI,P.Z.H., 1969. Ibid 20:391.

11. LEGATOWA, B., HORDYNSKA, S., KASZYCA, A., ROCZNIKI, P.Z.H., 1970. Ibid 21:21.

12. WIERZCHOWSKI, J. and NABRZYSKI, M.,Badania nad oznaczaniem śladowych ilości rtęci w niektórych produktach spozywczych. To be published in "Bromatologia i Chemia Toksykologiczna" (in press).

13. LUNDHOLM, B., 1966. The mercury problem. Symposium of the Swedish Royal Commission of Natural Resources. Stockholm.