

## **RISK ASSAY OF PHATOLOGIES FROM METHIL-MERCURY AND HEXACLHORO BENZENE IN A HIGH INDUSTRIAL DENSITY ZONE IN SICILY**

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### **ABSTRACT.**

The industrial area of the triangle Augusta, Priolo, Melilli in the South East Sicily at present hosts five refineries. A so high concentration of industry in a quite small area gives serious environmental pollution problems and can compromise the health of the local population. Releasing of polluters, due to a not rational disposal of waste water and to the not blasting of the polluting emissions in the environmental matrices, in which air, water and soil, expose the population to hazardous substances among that mercury and hexachlorobenzene; especially according to some studies, concentration of mercury and hexachlorobenzene several time higher than low limit was found on the Augusta bay. The compromising of the chain comes from proved accumulating of methyl-mercury in fish, widely consumed by local inhabitants. Epidemiological surveying demonstrate that the rate mortality standardized for congenital malformations in the male sex exceeds a lot the national value with one high statistic significance ( $p < 0.01$ ). Beginning a study in order to characterize the single relationship between each specific polluting and the pathologies was necessary. So the total mercury and methylmercury in hair of Augusta people and Catania controls and of the mothers of the last born children (in Augusta e in Catania) was determined comparing values coming from controls. For the hexachlorobenzene effect maternal milk samples coming from the mothers of the last born were analysed and confronted with the related controls. The outcomes will be an important start point to elaborate a fast and specifies methodical for assay poisoning.

### **INTRODUCTION.**

Very industrialized areas give to population the problem of exposure to different kinds of polluters, which have negative effects on health, though, some of them still to be assessed. The area we have studied hosts an out of proportion number of industries, situated over a relatively small surface. It presents a proven pollution by Mercury (Hg), Hexa-chloro-benzene (HCB) and Poly-chloro-biphenyls (PCB). As a consequence, a rapid and effective technique has been utilised to test Augusta population exposure to organic Hg, to HCB and PCB. Hg, both, in its inorganic and organic form (methyl-mercury  $\text{CH}_3\text{Hg}^+$ ), constitutes a potent environment polluter. It can be introduced in the environment through anthropic action as an inorganic substance because of bad disposal by industries which use it in processes of various nature (e.g.: catalysis of vinyl chloride synthesis, in chloral-soda systems, etc.). In atmosphere it is rapidly oxidized to its bivalent form ( $\text{Hg}^{2+}$ ); from there it falls back into water ecosystems or on the ground. Its passage into water can happen, as in our study, through illegal direct income using the normal piping for disposal of industrial discarded material. In water environment, where it precipitates in the sediment, it is made organic as  $\text{CH}_3\text{Hg}^+$  by bacteria.

It comes up, through primary and secondary producers and consumers, along the food chain. It gets to man through fishes and undergoing bio-magnification. It is very harmful to human health being a teratogen and mutagen agent.

Damages caused to human health can be of different degree. The greatest are those due to intrauterine exposure (1), since it crosses the placental barrier; it succeeds also in crossing the hemato-encephalic barrier causing damages mainly of neurological nature which depend on the exposure degree (4). Many others are the effects linked to Hg exposure, like renal damages and cardiovascular damages. The WHO classifies  $\text{CH}_3\text{Hg}^+$  as possible cancerous (5). HCB and PCB are numbered among potential endocrine chemical disrupters (EDCs), together with other substances like dioxins, furans, and phyto-estrogens (6). According to OECD (Organisation for Economic Co-operation and Development) (7):

- an "endocrine disrupter" is an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine function
- a "potential endocrine disrupter" is an exogenous substance that possesses properties that might be expected to lead to endocrine disruption in an intact organism.

Endocrine disrupters can be found at various levels of the alimentary chain, both in vertebrates (above all in raptors) and in invertebrates (8). Through consumption of contaminated food (meat, milk (9) and, in our case, fish) man comes in contact with such substances, which produce on his health effects of various type. Among those we find Endometriosis, early puberty, prostate cancer etc. According to some sources (6,10) there could be a correlation between hypospadias and exposure to environmental neuro-endocrine disrupters, being development of male genitals under hormonal influence.

## **BACKGROUND.**

The industrial area considered in the study is localized in the South-eastern area of Sicilian territory, on three different municipalities of the Siracusa province: Augusta, Priolo Gargallo and Melilli. Its Augusta port overlooks the Mediterranean sea. Peculiarity of the area is due to the presence of numerous wharfs localized along the whole coast also outside the port infrastructures. To be more specific, on a surface of just 16 Km<sup>2</sup> there are approximately 60 industrial settlements most of them being petrochemical ones.

The 2003 environmental analysis on sea sediments and fauna shows in our study area severe contamination from Hg, HCB and PCB. Moreover, both in sediments and in fishes and benthic fauna the trend of mercury and other above-named pollutants is very much comparable.

By monitoring the population of the Siracusa province from 1995 to 2002, we conclude that the Standardized Mortality Rate in males due to congenital malformations (SMR calculated as observed deaths / expected deaths x 100) for the Augusta Municipality exceeds by far the national and the regional value, with high statistic significance ( $p < 0.01$ ).

The Augusta population, and the other populations living by the rivers in the area, are exposed, through contaminated fish consumption, to a twofold risk: the one from exposure to Hg and that from exposure to neuro-endocrine disrupters (HCB and PCB). We have got ready a fast and simple system to estimate Hg and HCB exposure. It consists

of a crossed analysis which requires using biomarkers of easy sampling and of low psychological impact on the subject. Hair has been analysed for mercury, while milk from last born mothers from the study area has been analysed for HCB and PCB. From monitoring births and analysis conducted on mothers, data will emerge to formulate hypothesis of correlation between the above-named malformations and exposure to such pollutants.

In the last forty year period, determination of traces of elements in human hair samples has become more and more popular method for monitoring exposure to environmental pollution, for evaluation of systemic poisoning, for assessing nutritional status and for diagnosing some pathologies (2). Hair analysis produces a permanent recording of traces of elements associated with normal or abnormal metabolism, and of elements, like heavy metals, which an organism exposed to pollution takes up.

Hair is essentially a cross-linked, partially crystalline, orientated polymeric network containing a number of functional groups (e.g. acidic, basic, and peptide bonds) which have the faculty of binding small molecules. Human hair consists of approximately 65-95% proteins, 15-35% water, 1-9% lipids. The mineral content of hair is from 0.25 to 0.95% . Both essential trace elements and heavy metal can be found in human hair.

What makes hair a zone of mercury accumulation is the tendency of the same one (both in its organic and inorganic form) to make stable complexes with Sulphur; this is found in numerous residuals of Cysteine being part of the primary structure of keratin.

Moreover, the material is incorporated in the structure in a definitive way; therefore, along the longitudinal axis we will find a permanent recording of the exposure sequence of the body to the substances which have chemical affinity for the structure of the hair and can become integral part of its molecular and cytological structure: mercury is between these (also in its organic form). Mercury is accumulated in human and in rat hair. Mercury incorporation in hair is an irreversible process (3).

## **METHODS.**

Our study is aimed at analyzing Hg content in hair from subjects living in Augusta compared to controls living in Catania. Hair sampling was done on 100 subjects from Augusta and 100 subjects from Catania. Hg cecking in hair of 200 last born mothers from Augusta and of 200 controls from Catania is on going. In milk of these two groups are also cecked Hg, PCB and HCB. Determination of total Hg and  $\text{CH}_3\text{Hg}^+$  were done by Atomic Absorption Spectrophotometry after sample mineralization (13).

Analysis of HCB and PCB congeners in milk is on going. It is done by ECD Gas-Chromatography determination after sample clean-up by solid phase extraction (14).

## **RESULTS.**

Study of  $\text{CH}_3\text{Hg}^+$ , HCB and PCB is not yet completed. We are still busy reading some of the results and getting more samples.

All together we have analyzed 20 hair samples taken from Augusta and 20 hair samples taken from Catania.

Results show that average of Hg in Augusta samples ( $0.169 \mu\text{g/g}$ ) is much higher than the Catania controls ( $0.033 \mu\text{g/g}$ ).

Other statistical values are as follows:

$$SD_{Augusta} = 0.098$$

$$SD_{Catania} = 0.025$$

$$SE_{Augusta} = 0.025$$

$$SE_{Catania} = 0.009$$

$$t = -3.401$$

$$p = 0.003$$

We can, then, conclude that the statistical difference between the two studied group is highly significant.

## COMMENTS AND CONCLUSIONS.

We can be satisfied with the results obtained up to so far. Firstly we have proven there is a very significant difference in hair mercury concentration between Augusta inhabitants and people staying outside Siracusa province.

As already explained, literature shows that its storing is, in most of the cases, due to contaminated fish consumption. This doesn't surprise if we consider data previously described.

Augusta inhabitants are exposed to very harmful pollution due to mercury and to other very toxic pollutants, which are teratogen and moreover very persistent in environmental matrices.

The part of the study still on going will enable us to understand if absorbed Hg is mainly  $CH_3Hg^+$  and if HCB and PCB are present in maternal milk.

As we know HCB and PCB are the main responsible for malformations.

If HCB and PCB were present in maternal milk, we could than study further their role compared to the Hg role.

There will be need of a definite case-control study of mothers of malformed children which on one side can enable us to make clear the connection between local fish consumption, storing of mercury, and incidence of malformation; and on the other side can clarify the role of HCB and PCB in those processes.

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