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Summary of the report

CHAPTER 1 - Introduction

36. This report responds to the request of the Governing Council (GC) of the United Nations Environment Programme (UNEP), through GC decision 21/5, that UNEP undertake a global assessment of mercury and mercury compounds, in cooperation with other members of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC), to be presented to the Governing Council at its 22nd session in 2003. The assessment would include contributions from Governments, intergovernmental and non-governmental organizations and the private sector, and cover a number of specific elements defined in the GC decision. These elements are covered as far as possible in the different chapters of the report.

37. As part of the implementation of GC decision 21/5, UNEP established a Global Mercury Assessment Working Group to assist in the drafting and finalization of this report, first through a comment round by mail, then through a meeting of the Working Group, which took place 9-13 September 2002 in Geneva, Switzerland. The Working Group was open-ended and consisted of members nominated by Governments, intergovernmental organizations and non-governmental organizations.

38. This report will be forwarded to the Governing Council for consideration at its 22nd session in February 2003. By having initiated the development of this assessment report, the Governing Council will have a better basis for considering if any international action on mercury is called for in order to promote environmentally sound management of mercury and its compounds. The report will contribute to increased awareness and understanding among decision makers of the major issues related to mercury and its compounds, thereby facilitating the debate on the issue at the next session of the Governing Council.

CHAPTER 2 – Chemistry

39. Mercury occurs naturally in the environment and exists in a large number of forms. Like lead or cadmium, mercury is a constituent element of the earth, a heavy metal. In pure form, it is known alternatively as "elemental" or "metallic" mercury (also expressed as Hg(0) or Hg^0). Mercury is rarely found in nature as the pure, liquid metal, but rather within compounds and inorganic salts. Mercury can be bound to other compounds as monovalent or divalent mercury (also expressed as Hg(I) and Hg(II) or Hg^{2+}, respectively). Many inorganic and organic compounds of mercury can be formed from Hg(II).

40. Elemental mercury is a shiny, silver-white metal that is a liquid at room temperature and is traditionally used in thermometers and some electrical switches. If not enclosed, at room temperature some of the metallic mercury will evaporate and form mercury vapours. Mercury vapours are colourless and odourless. The higher the temperature, the more vapours will be released from liquid metallic mercury. Some people who have breathed mercury vapours report a metallic taste in their mouths.

41. Mercury is mined as mercuric sulphide (cinnabar ore). Through history, deposits of cinnabar have been the source ores for commercial mining of metallic mercury. The metallic form is refined from mercuric sulphide ore by heating the ore to temperatures above 540 ° C. This vaporises the mercury in the ore, and the vapours are then captured and cooled to form the liquid metal mercury.

42. Inorganic mercuric compounds include mercuric sulphide (HgS), mercuric oxide (HgO) and mercuric chloride ($HgCl_2$). These mercury compounds are also called mercury salts. Most inorganic mercury compounds are white powders or crystals, except for mercuric sulphide, which is red and turns black after exposure to light. Some mercury salts (such as $HgCl_2$) are sufficiently volatile to exist as an atmospheric gas. However, the water solubility and chemical reactivity of these inorganic (or divalent) mercury gases lead to much more rapid deposition from the atmosphere than for elemental mercury. This results in sig-

nificantly shorter atmospheric lifetimes for these divalent mercury gases than for the elemental mercury gas.

43. When mercury combines with carbon, the compounds formed are called "organic" mercury compounds or organomercurials. There is a potentially large number of organic mercury compounds (such as dimethylmercury, phenylmercury, ethylmercury and methylmercury); however, by far the most common organic mercury compound in the environment is methylmercury. Like the inorganic mercury compounds, both methylmercury and phenylmercury exist as "salts" (for example, methylmercuric chloride or phenylmercuric acetate). When pure, most forms of methylmercury and phenylmercury are white crystalline solids. Dimethylmercury, however, is a colourless liquid.

44. Several forms of mercury occur naturally in the environment. The most common natural forms of mercury found in the environment are metallic mercury, mercuric sulphide, mercuric chloride, and methylmercury. Some micro-organisms and natural processes can change the mercury in the environment from one form to another.

45. Elemental mercury in the atmosphere can undergo transformation into inorganic mercury forms, providing a significant pathway for deposition of emitted elemental mercury.

46. The most common organic mercury compound that micro-organisms and natural processes generate from other forms is methylmercury. Methylmercury is of particular concern because it can build up (bioaccumulate and biomagnify) in many edible freshwater and saltwater fish and marine mammals to levels that are many thousands of times greater than levels in the surrounding water.

47. Methylmercury can be formed in the environment by microbial metabolism (biotic processes), such as by certain bacteria, and by chemical processes that do not involve living organisms (abiotic processes). Although, it is generally believed that its formation in nature is predominantly due to biotic processes. Significant direct anthropogenic (or human generated) sources of methylmercury are currently not known, although historic sources have existed. Indirectly, however, anthropogenic releases contribute to the methylmercury levels found in nature because of the transformation of other forms. Examples of direct release of organic mercury compounds are the Minamata methylmercury-poisoning event that occurred in the 1950's where organic mercury by-products of industrial-scale acetaldehyde production were discharged in the local bay, and the Iraqi poisoning events where wheat treated with a seed dressing containing organic mercury compounds were used for bread. Also, new research has shown that methylmercury can be released directly from municipal waste landfills (Lindberg *et al.*, 2001) and sewage treatment plants (Sommar *et al.*, 1999), but the general significance of this source is still uncertain.

48. Being an element, mercury cannot be broken down or degraded into harmless substances. Mercury may change between different states and species in its cycle, but its simplest form is elemental mercury, which itself is harmful to humans and the environment. Once mercury has been liberated from either ores or from fossil fuel and mineral deposits hidden in the earth's crust and released into the biosphere, it can be highly mobile, cycling between the earth's surface and the atmosphere. The earth's surface soils, water bodies and bottom sediments are thought to be the primary biospheric sinks for mercury.

Mercury exists in the following main states under natural conditions

- As metallic vapour and liquid/elemental mercury;
- Bound in mercury containing minerals (solid);
- As ions in solution or bound in ionic compounds (inorganic and organic salts);
- As soluble ion complexes;
- As gaseous or dissolved non-ionic organic compounds;
- Bound to inorganic or organic particles/matter by ionic, electrophilic or lipophilic adsorption.

Significance of mercury speciation

49. The different forms mercury exists in (such as elemental mercury vapour, methylmercury or mercuric chloride) are commonly designated "species". As mentioned above, the main groups of mercury species are elemental mercury, inorganic and organic mercury forms. Speciation is the term commonly used to represent the distribution of a quantity of mercury among various species.

50. Speciation plays an important part in the toxicity and exposure of mercury to living organisms. Among other things, the species influence:

- The physical availability for exposure - if mercury is tightly bound to in-absorbable material, it cannot be readily taken up (e.g. into the blood stream of the organism);
- The internal transport inside the organism to the tissue on which it has toxic effects - for example the crossing of the intestinal membrane or the blood-brain barrier;
- Its toxicity (partly due to the above mentioned);
- Its accumulation, bio-modification, detoxification in – and excretion from – the tissues;
- Its bio-magnification on its way up the trophic levels of the food chain (an important feature particularly for methylmercury).

51. Speciation also influences the transport of mercury within and between environmental compartments including the atmosphere and oceans, among others. For example, the speciation is a determining factor for how far from the source mercury emitted to air is transported. Mercury adsorbed on particles and ionic (e.g. divalent) mercury compounds will fall on land and water mainly in the vicinity of the sources (local to regional distances), while elemental mercury vapour is transported on a hemispherical/global scale making mercury emissions a global concern. Another example is the so-called "polar sunrise mercury depletion incidence", where the transformation of elemental mercury to divalent mercury is influenced by increased solar activity and the presence of ice crystals, resulting in a substantial increase in mercury deposition during a three month period (approximately March to June).

52. Moreover, speciation is very important for the controllability of mercury emissions to air. For example, emissions of inorganic mercuric compounds (such as mercuric chloride) are captured reasonably well by some control devices (such as wet-scrubbers), while capture of elemental mercury tends to be low for most emission control devices.

CHAPTER 3 – Toxicology

53. The toxicity of mercury depends on its chemical form, and thus symptoms and signs are rather different in exposure to elemental mercury, inorganic mercury compounds, or organic mercury compounds (notably alkylmercury compounds such as methylmercury and ethylmercury salts, and dimethylmercury). The sources of exposure are also markedly different for the different forms of mercury. For alkylmercury compounds, among which methylmercury is by far the most important, the major source of exposure is diet, especially fish and other seafood. For elemental mercury vapour, the most important source for the general population is dental amalgam, but exposure at work may in some situations exceed this by many times. For inorganic mercury compounds, diet is the most important source for the majority of people. However, for some segments of populations, use of skin-lightening creams and soaps that contain mercury, and use of mercury for cultural/ritualistic purposes or in traditional medicine, can also result in substantial exposures to inorganic or elemental mercury.

54. While it is fully recognised that mercury and its compounds are highly toxic substances for which potential impacts should be considered carefully, there is ongoing debate on how toxic these substances, especially methylmercury, are. New findings during the last decade indicate that toxic effects may be taking place at lower concentrations than previously thought, and potentially larger parts of the global population may be affected. As the mechanisms of subtle toxic effects – and proving whether such effects are taking place – are extremely complex issues, a complete understanding has so far not been reached on this very important question.

Methylmercury

55. Of the organic mercury compounds, methylmercury occupies a special position in that large populations are exposed to it, and its toxicity is better characterized than that of other organic mercury compounds. Within the group of organic mercury compounds, alkylmercury compounds (especially ethylmercury and methylmercury) are thought to be rather similar as to toxicity (and also historical use as pesticides), while other organic mercury compounds, such as phenylmercury, resemble more inorganic mercury in their toxicity.

56. Methylmercury is a well-documented neurotoxicant, which may in particular cause adverse effects on the developing brain. Moreover, this compound readily passes both the placental barrier and the blood-brain barrier, therefore, exposures during pregnancy are of highest concern. Also, some studies suggest that even small increases in methylmercury exposures may cause adverse effects on the cardiovascular system, thereby leading to increased mortality. Given the importance of cardiovascular diseases worldwide, these findings, although yet to be confirmed, suggest that methylmercury exposures need close attention and additional follow-up. Moreover, methylmercury compounds are considered possibly carcinogenic to humans (group 2B) according to the International Agency for Research on Cancer (IARC, 1993), based on their overall evaluation.

Elemental mercury and inorganic mercury compounds

57. The main route of exposure for elemental mercury is by inhalation of the vapours. About 80 percent of inhaled vapours are absorbed by the lung tissues. This vapour also easily penetrates the blood-brain barrier and is a well-documented neurotoxicant. Intestinal absorption of elemental mercury is low. Elemental mercury can be oxidized in body tissues to the inorganic divalent form.

58. Neurological and behavioural disorders in humans have been observed following inhalation of elemental mercury vapour. Specific symptoms include tremors, emotional lability, insomnia, memory loss, neuromuscular changes, and headaches. In addition, there are effects on the kidney and thyroid. High exposures have also resulted in death. With regard to carcinogenicity, the overall evaluation, according to IARC (1993), is that metallic mercury and inorganic mercury compounds are not classifiable as to carcinogenicity to humans (group 3). A critical effect on which risk assessment could be based is therefore the neurotoxic effects, for example the induction of tremor. The effects on the kidneys (the renal tubule) should also be considered; they are the key endpoint in exposure to inorganic mercury compounds. The effect may well be reversible, but as the exposure to the general population tends to be continuous, the effect may still be relevant.

Summary of effect levels

59. To put the level of exposures for methylmercury in perspective, for the most widely accepted non-lethal adverse effect (neurodevelopmental effects), the United States (US) National Research Council (NRC, 2000) has estimated the benchmark dose (BMD) to be 58 micrograms per litre (µg/l) total mercury in cord blood (or 10 micrograms per gram (µg/g) total mercury in maternal hair) using data from the Faroe Islands study of human mercury exposures (Grandjean et al., 1997). This BMD level is the lower 95% confidence limit for the exposure level that causes a doubling of a 5% prevalence of abnormal neurological performance (developmental delays in attention, verbal memory and language) in children exposed in-utero in the Faroe Islands study. These are the tissue levels estimated to result from an average daily intake of about 1 µg methylmercury per kg body weight per day (1 µg/kg body weight per day).

60. Other adverse effects have been seen in humans with less reliability or at much higher exposures. For methylmercury, effects have been seen on the adult nervous system, on cardiovascular disease, on cancer incidence and on genotoxicity. Also, effects have been reported on heart rate variability and blood pressure in 7 year-old children exposed prenatally, and on cardiovascular mortality in adults. For elemental mercury and inorganic mercury compounds, effects have been seen on: the excretion of low molecular weight proteins; on enzymes associated with thyroid function; on spontaneous abortion rates; genotoxicity; respiratory system; gastrointestinal (digestion) system; liver; immune system; and the skin.

Dietary considerations

61. Fish are an extremely important component of the human diet in many parts of the world and provide nutrients (such as protein, omega-3 fatty acids and others) that are not easily replaced. Mercury is a major threat to this food supply. Certainly, fish with low methylmercury levels are intrinsically more healthful for consumers than fish with higher levels of methylmercury, if all other factors are equal.

62. There is limited laboratory evidence suggesting that several dietary components might reduce (e.g. selenium, vitamin E, omega-3 fatty acids) or enhance (e.g. alcohol) mercury's toxicity for some end-points. However, conclusions cannot be drawn from these data at this time.

CHAPTER 4 - Current mercury exposure and risk evaluations for human health

63. As mentioned earlier, the general population is primarily exposed to methylmercury through the diet (especially fish) and to elemental mercury vapours due to dental amalgams. Depending on local mercury pollution load, substantial additional contributions to the intake of total mercury can occur through air and water. Also, personal use of skin-lightening creams and soaps, mercury use for religious, cultural and ritualistic purposes, the presence of mercury in some traditional medicines (such as certain traditional Asian remedies) and mercury in the home or working environment can result in substantial elevations of human mercury exposure. For example, elevated air levels in homes have resulted from mercury spills from some old gas meters and other types of spills. Also, elevated mercury levels in the working environment have been reported for example in chlor-alkali plants, mercury mines, thermometer factories, refineries and dental clinics, as well as in mining and manufacturing of gold extracted with mercury. Additional exposures result from the use of Thimerosal/Thiomersal (ethylmercury thiosalicylate) as a preservative in some vaccines and other pharmaceuticals. The relative impacts of mercury from local pollution, occupational exposure, certain cultural and ritualistic practices and some traditional medicines may today vary considerably between countries and regions in the world, and are significant in some regions.

64. The chapter gives examples of data on total mercury and methylmercury exposures primarily from fish diets, but also other sources in different parts of the world, including Sweden, Finland, the United States of America (USA), the Arctic, Japan, China, Indonesia, Papua New Guinea, Thailand, Republic of Korea, Philippines, the Amazonas and French Guyana. For example, in a study of a representative group of about 1700 women in the USA (aged 16-49 years) for years 1999-2000, about 8 percent of the women had mercury concentrations in blood and hair exceeding the levels corresponding to the US EPA's reference dose (an estimate of a safe dose). As shown in the chapter, data indicate exposures are generally higher in Greenland, Japan and some other areas as compared to the USA.

65. In some of these countries and areas, local and regional mercury depositions have affected the mercury contamination levels over the years and countermeasures have been taken during the last decades to reduce national emissions. Mercury emissions are, however, distributed over long distances in the atmosphere and oceans. This means that even countries with minimal mercury emissions, and other areas situated remotely from dense human activity, may be adversely affected. For example, high mercury exposures have been observed in the Arctic far distances from any significant sources.

66. Data on mercury concentrations in fish have been submitted from a number of nations and international organisations. Additionally, many investigations of mercury levels in fish are reported in the literature. Submitted data, giving examples of mercury concentrations in fish from various locations in the world, are summarised in the chapter. The mercury concentrations in various fish species are generally from about 0.05 to 1.4 milligrams of mercury per kilogram of fish tissue (mg/kg) depending on factors such as pH and redox potential of the water, and species, age and size of the fish. Since mercury biomagnifies in the aquatic food web, fish higher on the food chain (or of higher trophic level) tend to have higher levels of mercury. Hence, large predatory fish, such as king mackeral, pike, shark, swordfish, walleye, barracuda, large tuna (as opposed to the small tuna usually used for canned tuna), scabbard and marlin, as well as seals and toothed whales, contain the highest concentrations. The available data indicate that mercury is present all over the globe (especially in fish) in concentrations that adversely affect

human beings and wildlife. These levels have led to consumption advisories (for fish, and sometimes marine mammals) in a number of countries, warning people, especially sensitive subgroups (such as pregnant women and young children), to limit or avoid consumption of certain types of fish from various waterbodies. Moderate consumption of fish (with low mercury levels) is not likely to result in exposures of concern. However, people who consume higher amounts of contaminated fish or marine mammals may be highly exposed to mercury and are therefore at risk.

CHAPTER 5 – Impacts of mercury on the environment

Build-up of mercury in food webs

67. A very important factor in the impacts of mercury to the environment is its ability to build up in organisms and up along the food chain. Although all forms of mercury can accumulate to some degree, methylmercury is absorbed and accumulates to a greater extent than other forms. Inorganic mercury can also be absorbed, but is generally taken up at a slower rate and with lower efficiency than is methylmercury. The biomagnification of methylmercury has a most significant influence on the impact on animals and humans. Fish appear to bind methylmercury strongly, nearly 100 percent of mercury that bioaccumulates in predator fish is methylmercury. Most of the methylmercury in fish tissue is covalently bound to protein sulfhydryl groups. This binding results in a long half-life for elimination (about two years). As a consequence, there is a selective enrichment of methylmercury (relative to inorganic mercury) as one moves from one trophic level to the next higher trophic level.

Bioaccumulation and biomagnification

The term **bioaccumulation** refers to the net accumulation over time of metals within an organism from both biotic (other organisms) and abiotic (soil, air, and water) sources.
The term **biomagnification** refers to the progressive build up of some heavy metals (and some other persistent substances) by successive trophic levels – meaning that it relates to the concentration ratio in a tissue of a predator organism as compared to that in its prey (AMAP, 1998).

68. In contrast to other mercury compounds the elimination of methylmercury from fish is very slow. Given steady environmental concentrations, mercury concentrations in individuals of a given fish species tend to increase with age as a result of the slow elimination of methylmercury and increased intake due to changes in trophic position that often occur as fish grow to larger sizes (i.e., the increased fish-eating and the consumption of larger prey items). Therefore, older fish typically have higher mercury concentrations in the tissues than younger fish of the same species.

69. The mercury concentrations are lowest in the smaller, non-predatory fish and can increase manyfold on the way up the food chain. Apart from the concentration in food, other factors affect the bioaccumulation of mercury. Of most importance are the rates of methylation and demethylation by mercury methylating bacteria (e.g., sulphate reducers). When all of these factors are combined, the net methylation rate can strongly influence the amount of methylmercury that is produced and available for accumulation and retention by aquatic organisms. As described in chapter 2, several parameters in the aquatic environment influence the methylation of mercury and thereby its biomagnification. While much is generally known about mercury bioaccumulation and biomagnification, the process is extremely complex and involves complicated biogeochemical cycling and ecological interactions. As a result, although accumulation/magnification can be observed, the extent of mercury biomagnification in fish is not easily predicted across different sites.

70. At the top levels of the aquatic food web are fish-eating species, such as humans, seabirds, seals and otters. The larger wildlife species (such as eagles, seals) prey on fish that are also predators, such as trout and salmon, whereas smaller fish-eating wildlife (such as kingfishers) tend to feed on the smaller forage fish. In a study of fur-bearing animals in Wisconsin, the species with the highest tissue levels of

mercury were otter and mink, which are top mammalian predators in the aquatic food chain. Top avian predators of aquatic food chains include raptors such as the osprey and bald eagle. Thus, mercury is transferred and accumulated through several food web levels (US EPA, 1997). Aquatic food webs tend to have more levels than terrestrial webs, where wildlife predators rarely feed on each other, and therefore the aquatic biomagnification typically reaches higher values.

Mercury compounds toxic to wildlife

71. Methylmercury is a central nervous system toxin, and the kidneys are the organs most vulnerable to damage from inorganic mercury. Severe neurological effects were already seen in animals in the notorious case from Minamata, Japan, prior to the recognition of the human poisonings, where birds experienced severe difficulty in flying, and exhibited other grossly abnormal behaviour. Significant effects on reproduction are also attributed to mercury, and methylmercury poses a particular risk to the developing fetus since it readily crosses the placental barrier and can damage the developing nervous system.

72. In birds, adverse effects of mercury on reproduction can occur at egg concentrations as low as 0.05 to 2.0 mg/kg (wet weight). Eggs of certain Canadian species are already in this range, and concentrations in the eggs of several other Canadian species continue to increase and are approaching these levels.

73. The levels of mercury in Arctic ringed seals and beluga whales have increased by 2 to 4 times over the last 25 years in some areas of the Canadian Arctic and Greenland. In warmer waters as well, predatory marine mammals may also be at risk. In a study of Hong Kong's population of hump-backed dolphins, mercury was identified as a particular health hazard, more than other heavy metals.

Vulnerable ecosystems

74. Recent evidence suggests that mercury is responsible for a reduction of micro-biological activity vital to the terrestrial food chain in soils over large parts of Europe – and potentially in many other places in the world with similar soil characteristics. Preliminary critical limits to prevent ecological effects due to mercury in organic soils have been set at 0.07-0.3 mg/kg for the total mercury content in soil.

75. On the global scale, the Arctic region has been in focus recently because of the long-range transport of mercury. However, impacts from mercury are by no means restricted to the Arctic region of the world. The same food web characteristics - and a similar dependence on a mercury contaminated food source - are found in specific ecosystems and human communities in many countries of the world, particularly in places where a fish diet is predominant.

76. Rising water levels associated with global climate change may also have implications for the methylation of mercury and its accumulation in fish. For example, there are indications of increased formation of methylmercury in small, warm lakes and in many newly flooded areas.

CHAPTER 6 – Sources and cycling of mercury to the global environment

77. The releases of mercury to the biosphere can be grouped in four categories:

- Natural sources - releases due to natural mobilisation of naturally occurring mercury from the Earth's crust, such as volcanic activity and weathering of rocks;
- Current anthropogenic (associated with human activity) releases from the mobilisation of mercury impurities in raw materials such as fossil fuels – particularly coal, and to a lesser extent gas and oil – and other extracted, treated and recycled minerals;
- Current anthropogenic releases resulting from mercury used intentionally in products and processes, due to releases during manufacturing, leaks, disposal or incineration of spent products or other releases;
- Re-mobilisation of historic anthropogenic mercury releases previously deposited in soils, sediments, water bodies, landfills and waste/tailings piles.