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PROPOSITION OF THRESHOLD FOR WASTE CONTAMINATED WITH MERCURY (COMPOUNDS) IN APPLICATION OF THE MINAMATA CONVENTION ON MERCURY AND IMPACT ASSESSMENT

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ABSTRACT: The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of mercury. Environmentally sound management of waste is under discussion. This note proposes a threshold for waste of category c) Contaminated with mercury or mercury compounds to be disposed of (Article 11 of the Convention), using the Globally Harmonized System of classification and labelling of chemicals of the United Nations (GHS - UNEP 2017). Mercury and mercury compounds are classified as substances for the physical, health and environmental hazards categories. The thresholds of mercury and mercury compounds classifying a mixture as hazardous for the different hazard categories (physical, health, environmental) are "Presence", >0.1% and >0.0025% (25 mg mercury/kg of waste) respectively. For impact assessment, this threshold is then compared with large data set of hazardous (793 data), potentially hazardous (depending on the concentration of hazardous substances) (55 data), as well as natural or non-polluted anthropized media (composts, sediments, agricultural soils) (21 784 data) from France. This demonstrates that 75% of the hazardous waste have higher total mercury concentration, that potentially hazardous waste samples have lower concentrations, and that all composts, agricultural soils and marine sediments and 99% of the fluvial sediments have lower concentrations. So, this threshold will not classify common industrial waste or natural media as requiring special treatment for safe disposal, but well a large part of industrial hazardous waste.

Keywords: concentration limit, GHS, ecotoxicity, environmentally sound management

1. INTRODUCTION

The Minamata Convention on Mercury (UNEP 2017) is a global treaty to protect human health and the environment from the adverse effects of mercury. Regular conference of the parties progress in technical recommendations to "make mercury history". Environmentally sound management of waste is one point under discussion.

The Convention defines in Article 11 "Mercury wastes":

“...2. For the purposes of this Convention, mercury wastes means substances or objects:

- (a) Consisting of mercury or mercury compounds;*
- (b) Containing mercury or mercury compounds; or*
- (c) Contaminated with mercury or mercury compounds,*

in a quantity above the relevant thresholds defined by the Conference of the Parties, in collaboration with the relevant bodies of the Basel Convention in a harmonized manner, that are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law or this Convention. This definition excludes overburden, waste rock and tailings from mining, except from primary mercury mining, unless they contain mercury or mercury compounds above thresholds defined by the Conference of the Parties...”

The scope of the paper is to provide a reliable concentration limit to the

Minamata Convention. This paper uses the Globally Harmonized System (GHS) of classification and labelling of chemicals of the United Nations to propose a threshold and compare it with concentrations observed in waste and natural media. The method is explained in detail in the paper, with a focus on ecotoxicity, which appears to be the property with the lowest dangerous ranking.

In this paper, the “concentration limit” used in the GHS is the equivalent of “threshold” of the Minamata Convention on Mercury, and “substance” used in the GHS is the equivalent of “compound” of the Minamata Convention on Mercury

2. MATERIAL AND METHODS

2.1 Properties of mercury and mercury substances in the GHS

It is proposed to use the Globally Harmonized System (GHS) of classification and labelling of chemicals of the United Nations (last version: UNEP 2017). The European Union has adopted the GHS system in 2008 (CLP 2008) and has developed an official list of the hazard properties of 4 249 substances, as well as a registration and self-classification system for producers and importers of chemical products (REACH system). This list is an Annex of the CLP regulation and can be downloaded in a spreadsheet template (CLP 2018) and is used here.

2.2 Particular case: Ecotoxicity in the GHS

The different categories of ecotoxicity are attributed to substances from experimental laboratory ecotoxicological standardized tests. Organisms are submitted to different concentration of the substance in their living medium, and the concentration producing 50% (or x %) of mortality or effect after a given time (called LC50 or EC50 or EC_x depending on test), or the highest concentration producing no observed effect (called NOEC) is measured. These concentrations expressed in mg of substance per liter of living medium are compared to concentrations of Table 1, and a category is attributed to the substance.

Table 1: Categories for substances hazardous to the aquatic environment for short-term (acute) and long-term (chronic) aquatic hazard (extract of Table 4.1.1 of GHS)

- (a) Short-term (acute) aquatic hazard
 - Category Acute 1: L(E)C₅₀ fish, crustacea, algae ≤ 1 mg/l
 - Category Acute 2: L(E)C₅₀ fish, crustacea, algae > 1 but ≤ 10 mg/l
 - Category Acute 3: L(E)C₅₀ fish, crustacea, algae > 10 but ≤ 100 mg/l
- (b) Long-term (chronic) aquatic hazard
 - (i) Non-rapidly degradable substances for which there are adequate chronic toxicity data available
 - Category Chronic 1: Chronic NOEC or EC_x fish, crustacea, algae ≤ 0.1 mg/l
 - Category Chronic 2: Chronic NOEC or EC_x fish, crustacea, algae ≤ 1 mg/l
 - (ii) Rapidly degradable substances for which there are adequate chronic toxicity data available
 - Category Chronic 1: Chronic NOEC or EC_x fish, crustacea, algae ≤ 0.01 mg/l
 - Category Chronic 2: Chronic NOEC or EC_x fish, crustacea, algae ≤ 0.1 mg/l
 - Category Chronic 3: Chronic NOEC or EC_x fish, crustacea, algae ≤ 1 mg/l

For substances with experimental results < 1 mg/l, the GHS uses multiplying factors called “M factors” to fine tune the classification of substances and mixtures with these substances. M factors are determined by the lowest L(E)C₅₀ and NOEC experimental values (Table 2). Mercury and mercury compounds are non-rapidly degradable compounds.

Table 2: Multiplying factors (M factors) for substances for highly toxic ingredients or mixture (categories Acute 1 and Chronic 1) (Table 4.1.5 of GHS)

Acute toxicity	M factor	Chronic toxicity	M factor	
L(E)C ₅₀ value (mg/l)		NOEC value (mg/l)	Non-rapidly degradable ingredients	Rapidly degradable ingredients
$0.1 < \text{CL(E)}_{50} \leq 1$	1	$0.01 < \text{NOEC} \leq 0.1$	1	-
$0.01 < \text{CL(E)}_{50} \leq 0.1$	10	$0.001 < \text{NOEC} \leq 0.01$	10	1
$0.001 < \text{CL(E)}_{50} \leq 0.01$	100	$0.0001 < \text{NOEC} \leq 0.001$	100	10
$0.0001 < \text{CL(E)}_{50} \leq 0.001$	1000	$0.00001 < \text{NOEC} \leq 0.0001$	1000	100
$0.00001 < \text{CL(E)}_{50} \leq 0.0001$	10000	$0.000001 < \text{NOEC} \leq 0.00001$	10000	1000
(continue in factor 10 intervals)		(continue in factor 10 intervals)		

Experimental ecotoxicity data of mercury and mercuric substances were taken from a reference UE publication (UE 2005).

The ecotoxicity of mixtures with ecotoxic substances at a given concentration can be assessed by the calculation rules presented at Table 3 (copy of Table 4.1.3 of the GHS).

Table 3: Classification of a mixture for short-term (acute) and long-term (chronic) hazard based on summation of the concentrations of classified ingredients (Tables 4.1.3 and 4.1.4 of GHS)

Category	Sum of the concentrations (in %) of ingredients classified as:	Mixture is classified as:
Short-term (acute) hazard	Acute 1 * M ≥ 25%	Acute 1
	(M*10*Acute 1) + Acute 2 ≥ 25%	Acute 2
	(M*100*Acute 1) + (10*Acute 2) + Acute 3 ≥ 25%	Acute 3
Long-term (acute) hazard	Chronic 1 * M ≥ 25%	Chronic 1
	(M*10*Chronic 1) + Chronic 2 ≥ 25%	Chronic 2
	(M*100*Chronic 1) + (10*Chronic 2) + Chronic 3 ≥ 25%	Chronic 3
	Chronic 1 + Chronic 2 + Chronic 3 + Chronic 4 ≥ 25%	Chronic 4

The European Union updated criteria on Ecotoxicity classification of waste (Regulation 997/2017, EU 2017). For simplicity of classification of waste with most of the time unknown mineral substances composition, this regulation does not use the multiplying factors M-factors (that are attributes of substances). M-factors were developed in the GHS to fine tune the ecotoxicity of ecotoxic substances (EC₅₀ or NOEC < 1 mg/L), and to avoid the creation of multiple of hazard statement codes to reflect the different grades of ecotoxicity. The resulting concentration limit for waste for chronic ecotoxicity for mercury and mercury compounds is 0.25% or 2500 mg/kg, hundred times higher than the concentration calculated here (see Results). Many experts believe that the abandonment of M factors for waste is irrelevant. This method has not been used here.

2.3 Data of concentration of mercury in waste and natural media

Data of hazardous waste, potentially hazardous waste and non-hazardous waste and natural media have been gathered:

- the concentrations of mercury, cadmium and lead in 793 hazardous waste (data from a hazardous waste management company) (Hennebert 2012);
- the 55 available data concentrations from an INERIS database for the following waste: car shredding residue (11), epoxy powder (1), excavated soil underlying a road (3), excavated soil (11), foundry sand (1), municipal solid waste incinerator bottom ash - MSWI BA (20), paint residue (1), phosphogypsum (2), sand blasting residue (1) and sand from incineration fluidized bed (4);
- the heavy metals in different composts (379 samples) from organic fraction of municipal wastes (separately collected or mechanically sorted) of 30 sites in France (Zdanevitch 2012);
- the results of routine quality monitoring of sediments (11 791 samples of fluvial sediments and 816 samples of marine sediments) of France by the Water Agencies (Padox and Hennebert 2010a, b);
- the data from routine analysis of agricultural soils (8 798 samples) are gathered at the French level by soil scientists (Gissol 2018).

3. RESULTS AND DISCUSSION

3.1 Properties of mercury and mercury substances in the GHS

The mercury and nine mercury substances from the list are presented at **Error! Reference source not found.** Two “generic entries” are also listed. Most frequently in waste, field measurement with fluorimeter and routine laboratory analysis will deliver total mercury concentrations (metallic or not) rather than mercury substances concentrations. If the exact mercury substances present in the waste is not known, which is frequently the case in waste, these “generic entries” are used in the EU (line 2 and 3 of the substances list in **Error! Reference source not found.**: “*inorganic compounds of mercury with the exception of mercuric sulphide and those specified elsewhere in this Annex*” and “*organic compounds of mercury with the exception of those specified elsewhere in this Annex*”). In total twelve entries are used for mercury and mercury substances, with their hazard statement codes (Hxxx).

Mercury and mercury substances are all classified Acute Toxic when the three routes (oral, dermal and inhalation) are considered, classified Specific Target Organ Toxic Single Exposure (1 substance: calomel) or Repeated Exposure (11 other substances), Ecotoxic Aquatic Acute Level 1 and Ecotoxic Aquatic Chronic Level 1. Additionally, mercury dichloride is classified mutagenic and reprotoxic, and elemental mercury is reprotoxic. Mercury difulminates and dimercy dicyanide dioxide are explosive (**Error! Reference source not found.**).

3.1.1 Classification of mercury and mercury substances (GHS, EU data) for ecotoxicity

Experimental ecotoxicity data of mercury and mercuric substances from a reference UE publication (UE 2005) are presented at Table 4. A summary can be found on the INERIS portal (INERIS 2018). The resulting M factors are most of the time 100 (with two values of 10 and two values of 1000 in a set of 12 values). It is proposed here to use $M = 100$ for acute and chronic ecotoxicity.

Table 4: Experimental L(E)C₅₀ and NOEC of mercury and mercury substances (UE 2005) and corresponding ecotoxicity level and multiplying factors (M factors)

Water	Fresh			Marine			Classification	
Ecotoxicity Organisms	Tests results (mg/L)	Ecotoxicity category (Table 2)	M factor (Table 3)	Tests results (mg/L)	Ecotoxicity category (Table 2)	M factor (Table 3)	Category	Proposed M factor
Acute	L(E)C ₅₀			L(E)C ₅₀				
Algae	0.010000	Acute 1	100	0.010000	Acute 1	100	Acute 1	100
Invertebrate	0.010000	Acute 1	100	0.003500	Acute 1	100		
Fish	0.000700	Acute 1	1000	0.070000	Acute 1	10		
Chronic	NOEC			NOEC				
Algae	0.000200	Chronic 1	100	0.000900	Chronic 1	100	Chronic 1	100
Invertebrate	0.000290	Chronic 1	100	0.000100	Chronic 1	1000		
Fish	0.000620	Chronic 1	100	0.005000	Chronic 1	10		

Using the calculation rules of Table 3 and the M factors obtained in Table 4, the concentration limits classifying a mixture containing mercury or mercury substances as ecotoxic acute and chronic are presented at Table 5. For full classification of mixtures, all the other ecotoxic substances must also be used, but this is not the question here. The level 3 has the lowest concentration: a mixture is hazardous if the concentration of mercury and/or mercury substances is greater than 0.0025% (mass/mass), or **25 mg/kg** (sometimes expressed as 25 parts per million – ppm). These concentrations are reported as concentration limit for Environmental hazard in **Error! Reference source not found..**

Table 5: Classification of a mixture for acute and chronic aquatic ecotoxicity based on summation of the concentrations of classified ingredients (source: UNEP 2017), containing mercury or mercury substances (M factor Acute and M factor Chronic = 100). In green: the lowest concentration limit

Level of ecotoxicity	Ecotoxic Acute if sum of	Ecotoxic (M=100) if sum of mercury substances	Acute sum of and	Ecotoxic Chronic if sum of	Ecotoxic Chronic (M=100) if sum of mercury substances
1	Acute 1 * M ≥ 25%	≥ 0.25%		Chronic 1 * M ≥ 25%	≥ 0.25%
2	(M*10*Acute 1) + Acute 2 ≥ 25%	≥ 0.025%		(M*10*Chronic 1) + Chronic 2 ≥ 25%	≥ 0.025%
3	(M*100*Acute 1) + (10*Acute 2) + Acute 3 ≥ 25%	≥ 0.0025% = 25 mg/kg		(M*100*Chronic 1) + (10*Chronic 2) + Chronic 3 ≥ 25%	≥ 0.0025% = 25 mg/kg
4	-			Chronic 1 + Chronic 2 + Chronic 3 + Chronic 4 ≥ 25%	≥ 25%

3.1.1 Proposed concentration limits for waste containing mercury or mercury compounds for physical, health and environmental hazard classification

The concentration limits are presented in the last row of **Error! Reference source not found..**, with the lowest by category of hazard in color. For human acute toxicity, concentration limits are derived from acute toxicity estimates for mixtures of the GHS. Some substances have specific concentration limits for some hazard class category in the EU list of substances, but they were not used here. For physical hazard, the requirement is “presence”. For health hazards, the lowest concentration is 0.1% of mercury or mercury substances in the mixture (Specific target organ toxicity, repeated exposure). For environmental hazard, the concentration limit is 0.0025% or **25 mg/kg**.

a. Concentration of mercury in different waste streams and natural media, and regulatory concentrations in sewage sludge and fertilizing products

Numerous data (> 22 000) from France, for different waste streams are compared with the proposed concentration limit:

- Hazardous waste (according to the EU List of Waste);
- Potentially hazardous waste (depending on the concentration of hazardous substances in it) (so-called “mirror entries” in the EU List of Waste), including municipal solid waste incinerator (MSWI) bottom ash, and
- Composts, sediments and agricultural soils.

Regulatory considerations on municipal sewage sludge (biosolids) and waste intended to be used as fertilizers are also presented.

More than 75% of the hazardous wastes have more than 25 mg Hg/kg. Data of Cd and Pb are presented, to illustrate that other hazardous elements are most of the time also present in these wastes.

Table 6: Classification of mercury and mercury substances with the GHS in the EU, and corresponding concentration limits classifying a mixture containing mercury or mercury substances as hazardous. In color: the lowest concentration limits for physical (brown), health (blue) and environmental (green) hazards

Hazard group		Physical		Health														Environmental			
Hazard Property		Explosive		Acute toxicity						Irritant			STOT*		Mutagenicity	Reproductive toxicity		Acute M=100	Chronic M=100		
				Oral			Dermal		Inhal.					SE						RE*	
				H300 Cat 2	H301	H302	H310 Cat 1	H311	H330 Cat 2	H331	H314	H315	H319	H335						H372	H373
Substances and hazard statement codes	CAS	H200	H201																		
mercury	7439-97-6									X					X			X		X	X
inorganic compounds of mercury with the exception of mercuric sulphide and those specified elsewhere in this Annex	-			X				X		X					X					X	X
organic compounds of mercury with the exception of those specified elsewhere in this Annex	-			X				X		X					X					X	X
dimethylmercury [1]; diethylmercury [2]	593-74-8 [1]; 627-44-1 [2]			X				X		X					X					X	X
dimercury dicyanide oxide; mercuric oxycyanide	1335-31-5		X		X				X		X				X					X	X
dimercury dichloride; mercurous chloride; calomel	10112-91-1					X							X	X	X					X	X
mercury dichloride; mercuric chloride	7487-94-7			X							X				X	X		X	X	X	X
2-methoxyethylmercury chloride	123-88-6				X						X				X					X	X
phenylmercury acetate	62-38-4				X						X				X					X	X
phenylmercury nitrate [1]; phenylmercury hydroxide [2]; basic phenylmercury nitrate [3]	55-68-5 [1]; 100-57-2 [2]; 8003-05-2 [3]				X						X				X					X	X
mercury difulminate; mercuric fulminate; fulminate of mercury	628-86-4	X			X				X		X				X					X	X
mercury difulminate; mercuric fulminate; fulminate of mercury [≥ 20 % phlegmatiser]	628-86-4		X		X				X		X				X					X	X
Concentration limits = thresholds	Hazardous if	Presence	Presence	≥ 0.25%	≥ 5%	≥ 25%	≥ 0.25%	≥ 15%	≥ 0.5%	≥ 10%	≥ 1%	≥ 10%	≥ 10%	≥ 20%	≥ 1%	≥ 0.1% lowest	≥ 1%	≥ 0.3%	≥ 3%	≥ 0.0025%	≥ 0.0025%

*STOT SE = specific target organ toxicity – single exposure, STOT RE = specific target organ toxicity – repeated exposure

Table 7: Distribution of Hg (in red: > proposed threshold of 25 mg Hg/kg), Cd and Pb in hazardous waste in France

Element	Hg	Cd	Pb
Number of data	793	2266	2856
Mean	7121	1272	6961
Min	0.1	0.0	1.1
1%	0.3	0.5	6.3
5%	10	2	40
10%	10	4	69
25%	190	14	162
50% = median	836	55	1758
75%	5336	129	3464
90%	12228	394	8907
95%	16835	2481	29192
99%	121368*	9725	101794*
Max	544018*	728708*	550423*

*probable analytical bias (X ray fluorescence analysis)

The Hg concentration for 55 potentially hazardous waste are presented at Figure 1 (left) and for MSWI BA at Figure 1 (right).

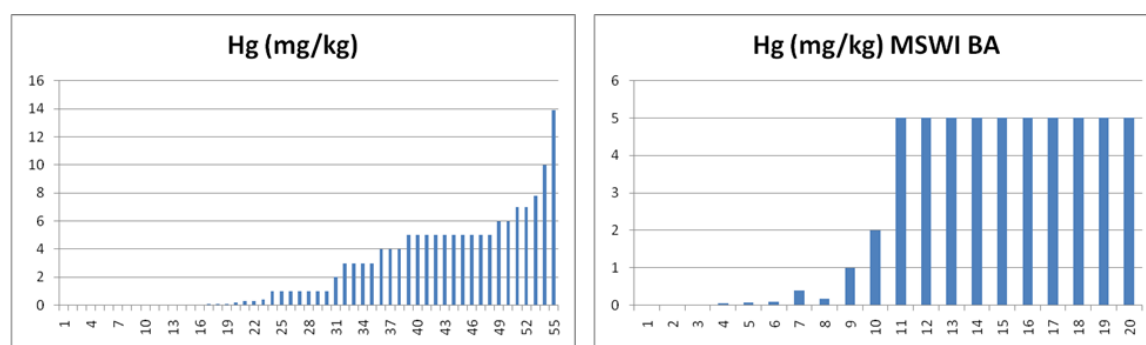


Figure 1: Distribution of total Hg concentration in 55 potentially hazardous waste (left), among which 20 samples of Municipal Solid Waste Incinerator Bottom Ash (right)

All the reported concentrations are lower than 25 mg/kg. For the MSWI BA, 8 samples have concentrations lower than the quantification limits of the laboratory (between 0.175 mg/kg and 5 mg/kg).

The distributions of Hg in different composts from organic fraction of municipal wastes (separately collected or mechanically sorted) of 30 sites in France (Zdanevitch 2012) are presented in Table 8.

The results of routine quality monitoring of sediments are joined to the table. The network aims to monitor pollution and hot spots are more intensively sampled. The regulatory concentration limits of Hg for these sediments for reuse in natural environment are 1 mg/kg and 0.8 mg/kg respectively. One percent of the fluvial sediments should be specifically managed for mercury, with the threshold of 25 mg/kg, and no marine sediment. These samples are contaminated by other heavy-metals (As, Cu, Cd, Pb, Zn - result not shown) and are in all the case identified in survey and separated during dredging.

Data from routine analysis of agricultural soils are presented (Gissol 2018). A detailed analysis is available (Baize et al 2007). Another publication deals among others with local geological “anomaly” of heavy metals (Baize 2000). According to the authors, the higher concentrations originates from the parent material of the soil (most of the case) or from industrial inputs. All the concentrations are lower than 25 mg/kg (Table 8).

Table 8: Concentration of Hg (mg/kg) in compost, fluvial and marine sediments, and agricultural soils (21 784 data) (in red: > proposed threshold of 25 mg Hg/kg)

Element	Compost	Fluvial sediments	Marine sediments	Agricultural soils
N samples	379	11 791	816	8798
Mean	0.39	1.22	0.50	0.08
Min	0.00	0.002	0.01	0.01
1%	0.02	0.005	0.02	
10%	0.09	0.03	0.05	0.02
25%	0.20	0.05	0.08	0.03
50% = median	0.30	0.13	0.13	0.05
75%	0.50	0.40	0.26	0.07
90%	0.80	1.30	0.53	0.11
99%	1.68	31.0	2.47	
Max	2.40	200	112	11.6

For municipal sewage sludge, the EEC Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (EEC 1986) (updated) states in its Annex I B the limit values for heavy-metal concentrations in sludge for use in agriculture for mercury: 16 to 25 mg/kg of dry matter. In France, the corresponding decree sets a concentration limit of 10 mg/kg of dry matter (RF 1998).

For reuse of waste as fertilizing products in the Circular Economy package (EC 2016), the EC has confirmed the concentrations of Hg in fertilizers, culture medium and soils improvers of 1 mg/kg and in one case 2 mg/kg, that are in the Regulation relating to fertilizers (EC 2003).

4. CONCLUSIONS

The Globally Harmonized System of the UN classifies mixtures with concentration of mercury and mercury substances as hazardous (aquatic acute and chronic ecotoxicity of level 3) if their concentration is greater than or equal to 0.0025%, or 25 mg/kg. This concentration limit could be used as threshold for disposal of waste of category "c" according to the Minamata Convention.

The impact assessment shows that this concentration will not classify any of the common industrial waste or composts, sediments of soils to be managed specifically for mercury, but well the hazardous waste, that are already stabilized or solidified before landfilling in special landfills for hazardous waste, and very few (1%) contaminated fluvial sediments (that in all the case are also contaminated with other heavy metals), according to French data. It is also consistent with the present concentration limits set in the EU for reuse of municipal sewage sludge and other waste as fertilizing products

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