CHAPTER 5

Application of the AMI Method for Comparative Assessment of Metals*

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Abstract

The AMI (Assessment of Mean Impact) method enables the comparative assessment of the impacts of toxic substances on aquatic ecosystems. It is based on three key principles: (1) For ecotoxicological endpoints, the method is based mainly on single-species laboratory EC50s (Effect Concentration for 50% of the individuals of a species), which is the endpoint with the lowest uncertainty and NOEC (No Observed Effect Concentration), a commonly used endpoint in long-term studies. (2) Instead of assuming a specific distribution, the median of the test results is applied for calculation of the ecotoxicity indicator. (3) The uncertainty of the ecotoxicity indicator is calculated using a distribution-free method.

This chapter briefly describes the method and focuses on its application for the assessment of impact of metals on aquatic species. For that purpose, 9 metals are considered in the analysis, sometimes tested wit different salt and speciation. Two interesting results can be highlighted: the toxicity of metals covers the whole range of toxicity of chemicals; the spread of EC50s for test results on metals is on average twice as great for metals compared with other chemicals. This increase in the variability of ecotoxicological responses from species is likely to be due to the change in bioavailability of metals associated with a change of test conditions (pH, or Organic Matter).

Keywords: aquatic ecosystem, LCIA, LCA, metals, speciation

Nota Bene: This chapter has been submitted in the early development of the researches, it does not reflect all the details and improvement of the AMI methods applying to inorganics.

Introduction and presentation of AMI

AMI is the ecotoxicological effect component of IMPACT 2002 (Impact assessment of chemical toxicants), a new method developed at the EPFL to determine the Life Cycle Impacts of Toxics.

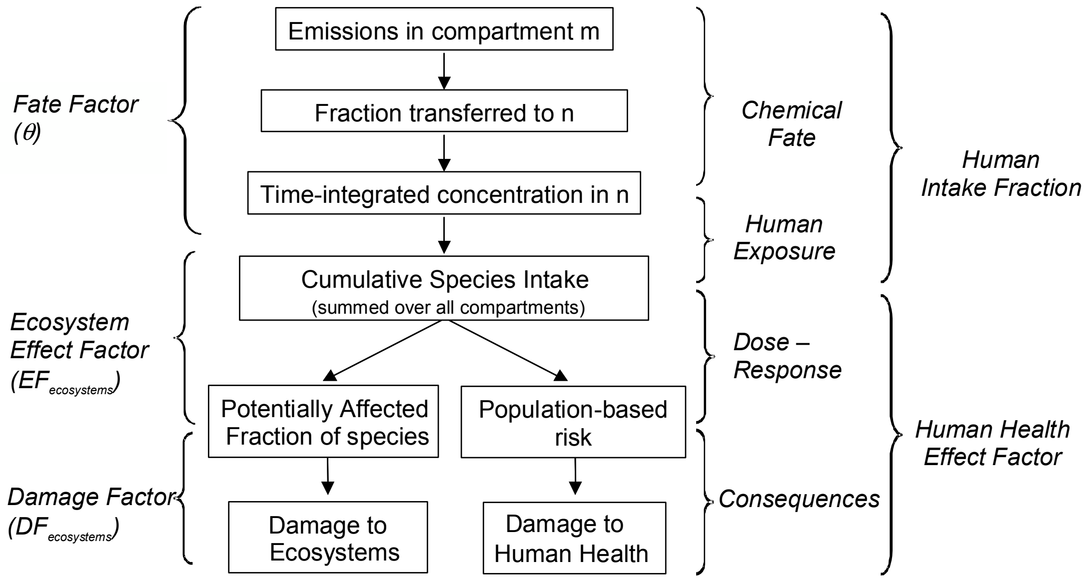

Figure 23: Impact 2002: general diagram

IMPACT 2002 provides a characterisation factor based on a generic default Effect Factor for chronic effects on aquatic (water column) ecosystems. Termed Ecotoxicological Damage Factor (EDF), it is calculated as the combination of two terms (Figure 23, lefthand side):

$$EDF = \theta \cdot EF_{ecosystem} \,.\, DF_{ecosystem} \qquad (1)$$

The fate factor θ consists of the equivalent residence time (the time- and space-integrated concentration in the aquatic freshwater per mass input of chemical released into the environment). The same fate model is applied as for human toxicity, but the interface between fate and effect is at the level of concentration for ecotoxicity. Exposure is implicitly taken into account in the Effect Factor.

The Effect Factor – EF – is the change in the Potentially Affected Fraction of species that experiences an increase in stress for a change in contaminant concentration.

Payet et al. (2002) proposed the AMI [Assessment of the Mean Impact] method to calculate ecotoxicological effect factors, along with estimates of the associated parameter (data) uncertainty. Effect Factors already exist for 300 chemicals. In the absence of field or mesocosm data, the use of median acute (LC50 or EC50) or median chronic (EC50) results of ecotoxicity tests for at least five species provides the preferable basis to estimate the median effect on multiple species systems (the median estimate of the $HC50_{EC50}$ which is the hazardous concentration of toxic affecting 50% of the species above their EC50). NOECs data does not provide a consistent basis for use in relative comparisons, hence is not retained except to estimate chronic EC50s via extrapolation. Both the median EC50 and the data uncertainty are estimated using a non-parametric (bootstrap) method to avoid unnecessary assumptions of the shape of a multiple species distribution (Species Sensitivity Distribution, SSD).

In short, the AMI method is based on three key principles: (1) For ecotoxicological endpoints, the method is based on single-species laboratory EC50s , which is the endpoint with the lowest uncertainty and NOECs (No Observed Effect Concentration), commonly used for endpoint in chronic studies. (2) Instead of assuming a specific distribution, the median of the test results is applied for calculation of the ecotoxicity indicator. (3) The uncertainty of the ecotoxicity indicator is calculated using a bootstrap method.

Application to metals

Metals are always present in the results of Life Cycle Inventory in Life Cycle Assessment and are often determinant in study results. Nevertheless, LCIA (Life Cycle Impact Assessment) methods for ecosystems so far do not enable reliable assessment of the toxicological impact on aquatic and terrestrial ecosystems. The toxicity is directly based on an NOEC [EDIP, 1997; USES-LCA 2000; ECO-INDICATOR 1999] or EC50 [AMI, 2002], without taking into account media conditions and the speciation of metals.

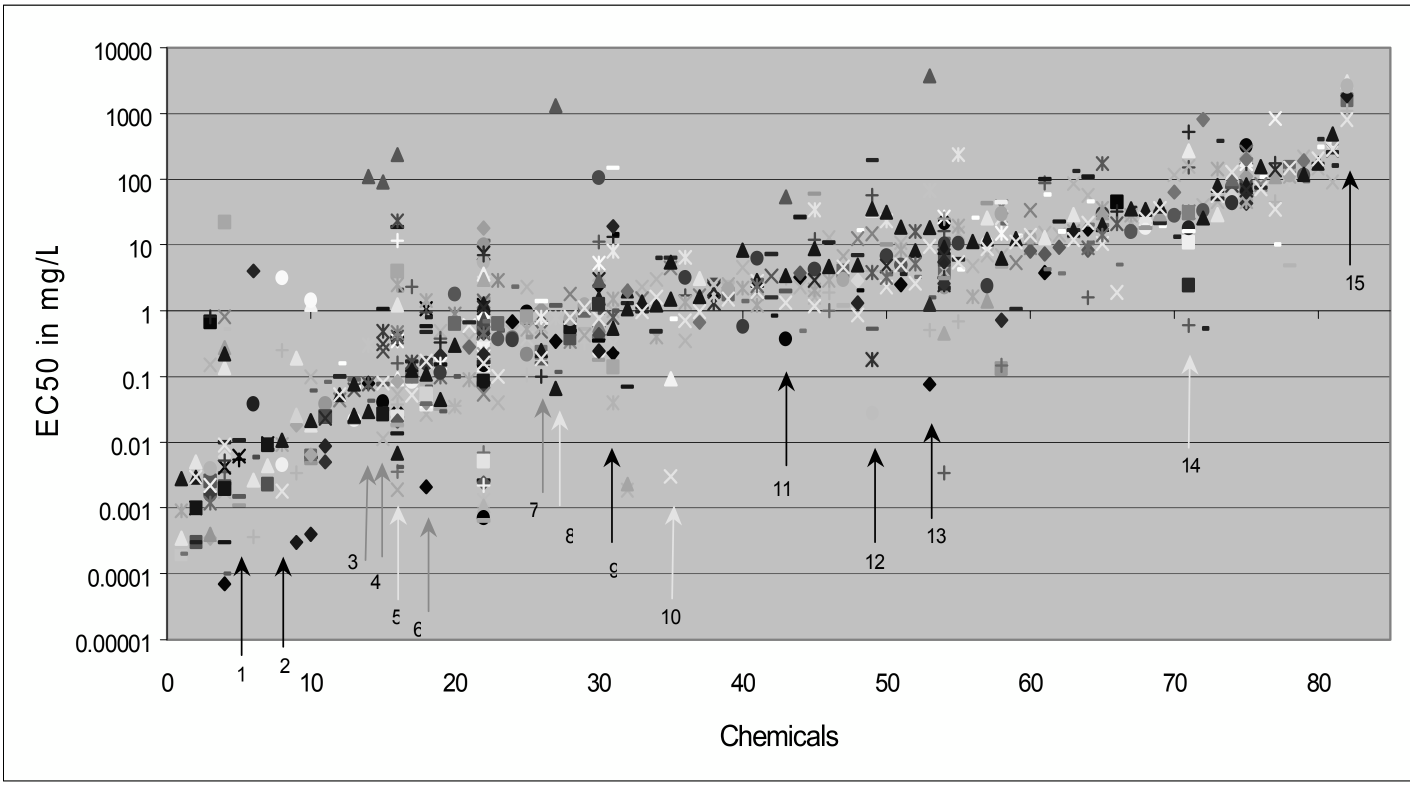

Figure 24: Comparison of the median toxicity of 82 chemicals based on 217 species. Arrows indicate the position of the following substances: Tributyltin (1); Silver (2); Copper (3) (4) (6) (7); Cadmium (5) (8) (10) (14); Zinc (9); Lead (11); Chromium (12); Nickel (13); Molybdenum (15).

The comparison between the toxicity of metals and non-metal substances, presented in Figure 24, illustrates three interesting points.

a) The metals presented here cover the whole range of chemical toxicity. From silver which have median toxicity (Median EC50 for at least 5 species) of 0.005 mg/L, to molybdenum (median EC50 = 1740 mg/L). The accuracy of metal toxicity data is therefore as important as for other chemicals.

b) The same metal can be tested with different salts, and these formulations may influence the toxicity. The examples of copper and cadmium are presented in Table 14. For cadmium, the most toxic formulation is 370 times more toxic than the least toxic.

c) The last point is the importance of the spread of the EC50 for test results on metals. The spread is on average twice as great for metals compared with other chemicals. As presented in Table 14, the ratio between the maximum and minimum EC50 can attain more than 5 orders of magnitude for cadmium, and approximately 4 orders of magnitude for chromium. An important factor of EC50 variability is explained by the differences in sensitivity between species and life stages of single species. Furthermore, concerning metal toxicity, an increase in the variability of ecotoxicological responses from species can be due to the different salt tested but also to the change in bioavailability of metals associated with a change of test conditions (pH, or Organic Matter).

Table 14: Toxicological results for 9 metals (results expressed in mg/L).

CASNO	**Salt**	**Speciation**	**Min EC50**	**Max EC50**	**Max/Min ratio**	**Median EC50**
10108-64-2	Cadmium chloride ($CdCl_2$)	CADMIUM II	2.000E-03	2.358E+02	1.238E+05	8.400E-0
7718-54-9	Nickel chloride (Cl_2Ni)	NICKEL II	7.700E-02	3.722E+03	4.866E+04	5.535E+0
10022-68-1	Cadmium nitrate Tetrahydrate ($CdH_8N_2O_{10}$	CADMIUM II	6.600E-02	1.307E+03	1.980E+04	5.610E-0
7447-39-4	Copper Chloride (Cl_2Cu)	COPPER II	1.100E-02	9.023E+01	7.915E+03	8.000E-0
7778-50-9	Potassium Dichromate ($Cr_2K_2O_7$)	CHROMIUM VI	2.800E-02	1.950E+02	7.040E+03	4.015E+0
7446-20-0	Sulfuric acid, zinc salt (1:1), heptahydrate ($H_{14}O_{11}SZn$)	ZINC II	4.000E-02	1.479E+02	3.698E+03	1.001E+0
10031-43-3	cupric nitrate trihydrate ($CuH_6N_2O_9$)	COPPER II	3.000E-02	1.090E+02	3.695E+03	7.800E-0
7761-88-8	Silver nitrate ($AgNO_3$)	SILVER I	2.000E-03	3.160E+00	1.756E+03	1.000E-0
7758-99-8	Copper Sulfate (pentahydrate)	COPPER II	2.000E-03	1.430E+00	6.842E+02	1.190E-0
10099-74-8	Lead nitrate	LEAD II	3.700E-01	5.390E+01	1.457E+02	2.565E+0
1461-22-9	Tributyltin Chloride	TRIBUTYLTIN	1.000E-03	1.080E-02	9.818E+00	5.000E-0
7631-95-0	Sodium molybdate	MOLYBDENUM VI	8.000E+02	3.057E+03	3.821E+00	1.740E+0

As presented in Figure 25, accuracy in the assessment of the toxicity of metals is crucial since the uncertainty is associated with the toxic value.

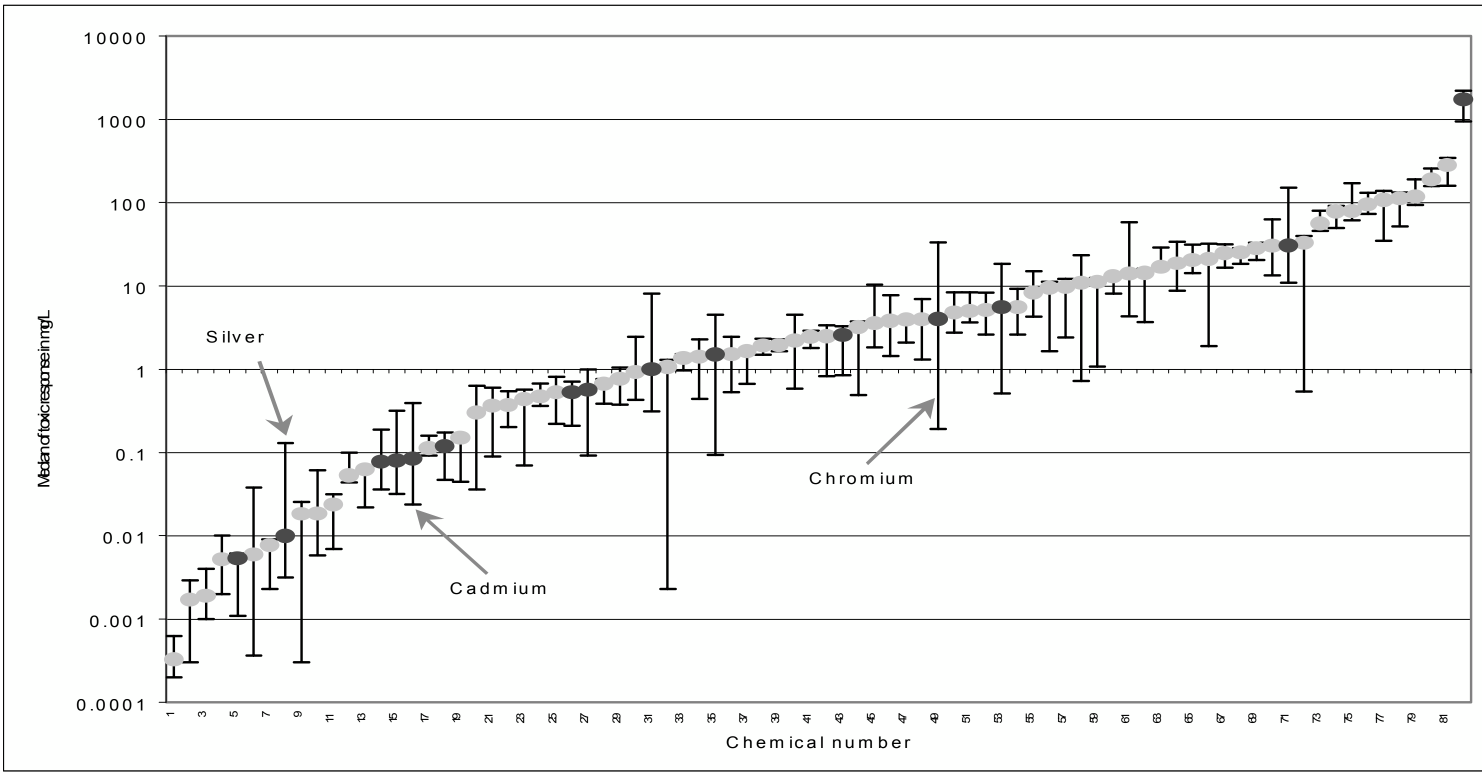

Figure 25: Median toxicity of 82 chemicals including 67 organics (grey dots) and 15 metals (black dots) ranked from most to least toxic. The associated uncertainty is calculated using the bootstrap technique as described in the AMI method [Payet et al, 2002].

Indeed, discrimination between the levels of toxicity of substances is particularly important in a comparative approach like LCA. A high degree of uncertainty in the assessment of toxicological impacts tends to reduce the interpretability of the final study results. It seems therefore important to better identify the effect of metal speciation, in order to improve the accuracy of the ecotoxicity indicator, which is used in the LCIA method.

Conclusions

The non parametric version of the AMI method and its integration in the IMPACT 2002 assessment framework offers interesting new insights for the comparative assessment of chemicals, for either LCIA or comparative risk assessment. Indeed, being close to the mode, the median is a good representative of the responses of the greater number of species. Furthermore, this estimator is not influenced by outliers and is a stable statistical estimator if sufficient data are considered. This is not right if the median is based on less than 5 EC50s. For three or four data for example, the gap between consecutive EC50s can be very large and the median, as a breakdown point indicator, would became unstable. Considering the confidence interval of the median, the bootstrap is a distribution-free method that fit the data spread. This is visible in Figure 25, where the asymmetry of the confidence interval follows the asymmetry of the EC50s spread. When a very sensitive species is tested while all other species present in average a good resistance to the substance, the confidence interval is skewed in favour of the lowest concentration. On the opposite, if the substance is in average very toxic for most of the species while only a small number are resistant, the confidence interval is skewed in favour of the high concentrations. The skewness of the distribution is therefore important in the description of the substances toxicity, and the only way to express this information is the use of a distribution-free method for the assessment of confidence intervals. Nevertheless, this is also likely to be a problem for small dataset or when a biological group of species is over-represented in the EC50s dataset for a substance. For the first point, the bootstrap based confidence interval requires at least 5 data and the calculation is not feasible for 3 or 4 species. For the second point, the over-representation of one phyla or taxa could lead to a biased estimate of the confidence interval excluding one whole phylum from the confidence interval of the median. In order to avoid it, three rules can be applied: (1) To require a minimum number of EC50s for the calculation of the Effect Factor (e.g.: a minimum of 5 EC50s or NOECs); (2) To fix a minimum diversity representation (e.g.: data covering at least three species from three different phyla or taxa); (3) To propose a flexible application of the confidence interval with some alternatives to the bootstrap (e.g. if the Geometric mean of one phyla is out of the range of the confidence interval, this geometric mean can be substituted to the confidence limit).

The application of the AMI method in its non-parametric version has provided interesting findings related to the comparative assessment of metals. Depending on the metal tested, the $HC50_{EC50}$ cover a broad range of toxicity (about 6 orders of magnitude between the highest and the lowest $HC50_{EC50}$), as variable as the organic toxics. Depending on the formulation tested, which is linked to the metal speciation, the $HC50_{EC50}$ can vary by more than two order of magnitude. The variability of EC50s for metals is in average twice greater than the variability of EC50s for organic substances, and this can also be due to the speciation of metals. Indeed, the metals toxicity is conditioned by the speciation, and the speciation depends on the media condition. Therefore, the variability in pH, organic matter, hardness, etc. is likely to influence considerably the toxicity of the substance. This is highlighted by the AMI method since the indicator is based on the average response of species. A method based on the most sensitive species like the PNEC would not allow such an observation since only the lowest EC50 or NOEC (the one based on the most toxic speciation) would be considered in the assessment, and therefore, metals would simply appear as very toxic substances.

In terms of perspectives, these results are highlighting the strength of a method based on the mean response of species for comparative purpose. It is therefore possible to have a better perception of the toxicity of metals compared to other substances. Furthermore, it allows to make a distinction regarding the media quality for the calculation of Effect Factors for metals. This would allow the development of a spatially differentiated Effect Factors database, relating the intensity of the impact to the quality of the ecosystems biotope.

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