# Dangerous substances from industrial activities. Emission estimation method for surface water concentration<sup>1</sup>.

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The emission factors in water streams of the priority and dangerous substances as defined by the EU directive, were estimated at plant end. The information existing in the literature, both technical and economic, and in the databank of local regulating authorities, was firstly examined to assure the confidence. All numerical data was then statistically treated. Two methods have been used depending on the available parameters: the first was utilised data of incoming water fluxes, substances concentration, together to the productivity data, the second goes thorough the number of workers and water demands. Data of the industries itself were thus compared and integrated with information on the process and the plant, verified and applied to the activity categories. The results can be used for authoritative examination, environment description and control, territorial plans.

## 1. Introduction

To get knowledge of the environment condition, it is cost-effective to collect data of different source. In Italy two kind of data sources exist: one is of the territorial administration offices like that of city, district, and region and the other is of the ambient agencies (like ARPA). For the surface water, the first type of inventory relates to the documents for the clearance to open an industrial activity. Each report lists the quantities of water necessary for the industrial processes (in-water) and of the emission (out-water) together to the parameters of water quality. They would thus indicate the concentrations of pollutant substances declared by the industry itself. The second type of document derived from chemical analyses of surface water samples collected during the inspections, inside the production place or outside. However the records are incomplete, very unmanageable, often untrustworthy. It is consequently necessary to collect the data and combine them with those deriving from the knowledge of the production processes. The aim of this work, is to get emission factors integrating the existing data with chemical and engineering data of a process layout, and together to data existing in world-wide available electronic banks or papers on environment, or LCA studies.

# 2. Methods

<sup>&</sup>lt;sup>1</sup> Updated part of that published in PTUA, All.8 of the Relazione Generale, November 2004, Regione Lombardia

Data on water status are sometime available in the regulatory acts required for the water industrial consume clearance together to the results of ARPA analysis.

However it may happens that the confidence of the data is low due to the modification of the technology on site and to the innovation. Only for few production processes it is possible to find data about the concentration of pollutants in the water fluxes of a plant. In such cases it is possible to determine the absolute quantity of the pollutants related to the process and make all estimation on environment impact. The concentration values are rarely available for several reason as the process complexity may be high or it may produce uncommon objects. More frequently reticence exists due to industrial secrets and commercial policy or to privacy aspects. We then estimated the emission factors relative to the dangerous substances using different methodologies depending on the available data. Two methods can be used: the first can be named "direct" because the procedure is straightforward (Figure 1).

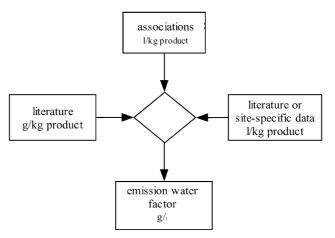


Fig.1. Direct method for the calculation of pollutant emission factor.

It needs the knowledge of production data for the specific plant because many pollutant charge are referred to the weight, the volume, the production unit<sup>2</sup>. Category association reports on productivity may be useful to this aim. However the data are scarcely available for a single unit due also to the small dimension of the great part of industrial sites, and to estimate them it needs a vast work of analysis of existing information after a systematic survey. Concentration data at the plant end, are similarly available if one knows the water quantities from the literature sources, technical reports of category association, LCA studies or, less accurately, by data of similar activities estimation.<sup>3</sup>. The second methodology for the water emission factors may involve the data having a good confidence, published by ISTAT on the number of employees in industry.

<sup>&</sup>lt;sup>2</sup> e.g. See the compared methodologies in EPA- EIIP-(Emission Inventory Improvement Program)

<sup>&</sup>lt;sup>3</sup> Production information have been considered using ATECO codex specified until to the 6° digit.

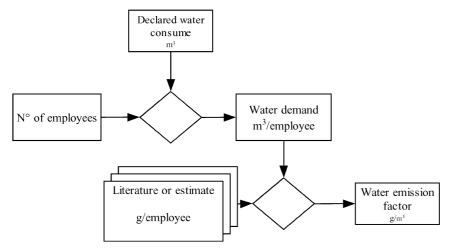


Fig. 2. Alternative two steps process for the water emission factor.

In fact considering the two entities that constitute the pollutant emission factor, the pollutant weight and the waste water fluxes, it is possible to calculate them referring, at first, to each employee. So one can obtain the value of the pollutant water charge for different production site simply by dividing the above two values. The two steps process reported in figure 2, needs the estimation of the water demand (m³ for each employee) which is by itself relevant for the control and ruling of the territory.

The estimation of the two parameter referred to each personnel is the key of this method. A relevant role can covered by the LCA studies and some other analysis like the collected data of Masterplan of the ITALCOPO group (1992; only for the activities with less than 20 persons) or case histories and technical papers.

If the confidence range is overcome, frequently the reason is that more than one process exist, and it is thus necessary to disaggregate the production information of the specific site into particular processes. It however necessary to consider a model process to know unavailable data. Emission factors were grouped following the official classification ATECO 2002<sup>4</sup> derived from the international NACE (Rev. 1.1). Such estimation may not strictly derive from the ATECO classification of that industry, which is attributed to the first activity, creating some problems for the arrangement of the data and consequently it is very troublesome to associate the pollution to a defined activity. On the contrary, if the correlation is reachable, it allows the deep evaluation of the pollution because it is possible "to name" a certain polluted water stream and to control it. As reverse production process can be identified from their water streams.

## 2. Results: the estimated parameters.

The vast number of information, both numerical data and alpha data, have been examined in the beginning of the study, to ascertain their confidence and the agreement

<sup>&</sup>lt;sup>4</sup> ISTAT Istituto Nazionale di Statistica classified all the activities in the document ATECO 2002 to adopt coherent statistical analyses. The base was the NACE Rev. 1.1, which is an EU Regulation n. 29/2002, published on the Official Journal of 10/1/2002

among those of the same ATECO class. Many quantitative data were biased, or not complete for the specified activity, often completely wrong. On the base of the process and plant knowledge of each activities and of the general description of the sector, new indication have been added by the authors. As a consequence, the information with the right ATECO classification were compared when possible, using the different data bank at disposition (CESTEC data bank was one of the most useful). Several data in a classification were therefore disaggregated and associated to different activities. Probably the non-corrected classification was due to the industry trade and technical evolution.

Tab. 1. Available and calculated emission factors and other significant parameters.

Name	Type	Unit	Source
Product water demand.	Water necessary for product unit	m <sup>3</sup> /kg (or product unit)	Literature-LCA
Substance concentration in water discharged.	Weight for volume of water discharged.	g/m³ (ppm)	Literature- LCA
Employee water demand.	Water utilization for employee	m <sup>3</sup> /employee	Estimation
Efficiency factor.	Charge diminution on treatment or other cause.	Fraction or %	Estimation
Production coefficient and synthesis.	Substance charge present in the product	g/m <sup>3</sup> (ppm)	Estimation
Emission factor on	Weight for unit of	g /kg (o product	Literature-LCA
production unit.	production.	unit)	Estimation
Emission factor on	Weight for unit of	g/employee	Estimation
employee unit	employee.	(* year)	
Emission factor on water emission unit.	Weight for unit of water discharged	μg/l	Estimation

A further examination was performed taking into account the process layout, P&I scheme, and the ARPA data; it allowed to name the water fluxes on their typology (cooling water, process water, meteoric or civil water fluxes).

The great effort made to validate the information was in part justified by the nature of data found in the data bank of the official institutions. In fact the companies are obliged to fulfil an information sheet that the regulatory offices mainly use to calculate the taxation or, more generally, the charge of economic imposition. It may thus happen that each data is forced toward the observance of regulatory acts in a sufficient manner more than to be technically determined. A problem of agreement may consequently exist between literature data and official data. Both were however considered at the same level of confidence. The validation effort was something not completely assured but it was stopped when the minimum of uncertainty was reached with the maximum of agreement among information. Only after the quality reinforcement of data, they were statistically treated.

Table 1 reports all the parameters that can be calculated managing the information and the data from several sources. Considering that the aim of the work is to evaluate the

diffusion of the priority and dangerous substances<sup>5</sup> and map the Lombardia territory, the most relevant parameters are those referred to each employee or product unit.

Tab. 2. Emission factor; ISTAT DG 24.1- base products of the chemical sector

Substances	D. lgs.	367/03	Emission factor	
	* Limits 2008 (µg/l)	Effort to comply**	(µg/l)	g/man year
Cd and derivatives	1	В	5,70E-01	3,14
C10-13-chloroalcanes	0,5	В	6,04E-02	33,2
1,2-Dichloethane	3	В	traces	1,51E-13
Dichloromethane	10	В	traces	traces
Esachlorobenzene	0,0003	A	3,87E-01	2,13
Esaclorobutadiene	0,01	M	3,87E-01	2,13
Esaclorocycloesane	0,002	M	3,87E-01	2,13
Pb and derivatives	2	В	8,51E-01	4,68
Hg and derivatives	0,05	В	1,58E-02	8,67E-02
Ni and derivatives	3	M	4,72	26
Nonylphenols	0,3	A	8,04E+01	45,8
(4-(para) -nonylphenol	0,01	A	8,04E+01	45,8
Octylphenols	0,1	A	8,04E+01	45,8
(para-t-octilphenol)	0,1	A	8,04E+01	45,8
Pentachlorobenzene	0,03	В	5,04E-02	0,28
Pentachlorophenol	0,1	В	traces	traces
PAH	0,02	A	6,52	35,8
Trichlorobenzene	0,1	n.d.	traces	traces
Trichloromethane	10	n.d.	traces	traces

\* G.U. 8/01/04 November 2003, Surface water; \*\* Author's evaluation of the effort need to reach the indicated values at 2008: B = low , M = 50% about percent probability because the real emissions are greater 1 to 3 order than those foreseen at 2008 ,A = high, a near to 3 greater order exist than those foreseen at 2008. \*\*\*The water demand /man (employee) was calculated at 5500 m<sup>3</sup>/y.

These really allow the easy evaluation of the environment impact on the surface water of a specific production site. With this direction in mind, the alternative two steps process for the water emission factor appears the more useful. The parameters relate to the plant end and one have to take in account many physical factor (efficiency or export factor) to calculate the substance concentration in the water surface course. One of these

<sup>&</sup>lt;sup>5</sup> 33 substances (see column 1, table 2) or group of substances are on the list of priority substances including selected existing chemicals, plant protection products, biocides, metals and other groups like Polyaromatic Hydrocarbons (PAH) that are mainly incineration by-products and Polybrominated Biphenylethers (PBDE) that are used as flame retardants (COM(2006)397 final)

factor may be e.g. the water treatment itself performed in the site. The efficiency factor was not considered here.

By the exam of the whole information it was possible to determine, at first, an useful matrix that links the substances emitted into surface water to the activity division as by ATECO. Table 2 reports the emission factor estimated for the ISTAT DG 24.1, activity sector which is the base products manufacture of the chemical sector.

## **Conclusions**

To compare the technical literature sheets and the data of the authoritative institutions is useful because the convergence among the different evaluations when associated to the correct interpretation of the variables, leads to a deep comprehension of the industrial process and associate pollution causes. Performing this work, the knowledge of the industrial process and plant is essential to allow the creation of a model from which estimate data when they are unavailable. The result is the estimation of emission factors. They are distinctive of a specific industrial activity and may be used to assess the environmental impact of anthropogenic activity and to characterises industrial zone. The more impacting production sector among those existing in a industrial zone may be also recognised At international level the estimation of the emission factor is today considered very useful (see EPA programs). The described methodologies depends on the available data; one of them needs the knowledge of the water demand (m³ for each employee) that is a useful parameters by itself.

The established data may be compared with the chemical analyses performed on the territory by public laboratories. This action is now approaching on the Lombardia region with the aim to validate the emission factor values. The methodologies here described can be moved also to calculate the emission factor pollutants other than the priority and dangerous substances, in different matrix too.

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