

## **Chlorinated solvents in drinking water in Lombardy: the need for and consequences of a change in Italian regulations**

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**Abstract** The current Italian regulations on water intended for human use is derived from the 80/778 EEC Directive. For chlorinated solvents (parameter no. 32), the maximum allowed concentration (MAC) is  $30 \mu\text{g l}^{-1}$ , which corresponds to the sum of the contaminants, but no limits have been established for any single compound. Chronic and acute toxicity greatly differs for chlorinated solvents (e.g. 1,2-dichloroethane vs perchloroethylene), and considering only the sum of individual concentrations results in an unsatisfactory evaluation of the potability of water. Individuals could be exposed to concentrations of single components exceeding the MAC established by the World Health Organization (WHO) or the current revision of the EEC Directive, under examination by the European Union (EU) Council. A close examination of the results of an analysis performed on more than 700 samples over seven years from wells in the Province of Varese highlights this issue and stresses the need for a rapid change of the Italian regulations. It is therefore desirable to take into account the toxicological potency of each individual compound rather than simply relying upon the sum of the concentrations of the contaminants.

### **INTRODUCTION**

The main principle used to evaluate the acceptability of water with regard to chemical parameters in Italy has been the presence versus the absence of a contaminant. The presence of chemical pollutants has required the establishment of acceptable limits of exposure, which have been determined by evaluating the chronic effects on humans following hypothetical lifetime exposures and assuming a consumption of  $2 \text{ l day}^{-1}$  of water. This method does not address the issues of short-term exposure and multiple exposure pathways. Table 1 shows the problems and possible answers associated with the establishment of chemical parameters of toxicological significance.

To improve our ability to characterize water quality, chemists have been working to improve analytical specificity and sensitivity, focusing on compounds that are normally present in very low concentrations. Bjørset (1981) illustrated the relationship between sensitivity, specificity and pharmacological knowledge (Fig. 1). Transferring this information to regulations is challenging.

**Table 1** Problems and answers associated with the establishment of chemical parameters of toxicological significance.

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**PROBLEMS**

- Toxicological knowledge
- Susceptibility of the host ( biological variability/hypersusceptibility):
  - age
  - immunological condition
  - enzymatic deficit
  - heredity
- Animal/human extrapolation
- Experimental vs environmental dose
- Quantification of effects
- Synergy effects
- Updating – revisions
- Evaluations:
  - single analysis
  - mean value ( time interval)
  - moving average (time interval)

**ANSWERS**

- Regulated parameters (on theoretical/scientific basis or practical/managerial basis)
  - Specific controls knowledge of sources/mechanism of pollution)
  - Identification of substitute parameters (TOC, AOX, Ames test)
  - Development of analytical techniques for organic compounds
  - Centralization and diffusion of biological/toxicological information
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On the basis of 15 years experience, this paper examines the Italian regulations for chlorinated solvents in drinking water and emphasizes the need for better health protection and more cost-effective regulations.

**ITALIAN REGULATIONS**

Up until 1985, Italy had no regulations on maximum acceptable contamination (MAC) for drinking water. The first attempt to establish MACs for the evaluation of water quality was made by the local government of Regione Lombardia in 1983 (Circular Letter no. 38/SAN/83), based on the EEC Directive no. 778/80, which was passed after finding serious and extensive contamination of groundwater due to chlorinated solvents. Two years later, a “Decreto del Presidente del Consiglio dei Ministri” (DPCM) was passed and in 1988, by means of the “Decreto del Presidente della Repubblica” (DPR) no. 236, the Italian Government adopted the EEC Directive 778/80. This directive identifies quality criteria for four organoleptic parameters, 15 physico-chemical parameters, 14 parameters concerning undesirable substances, six microbiological parameters and four supplementary parameters for water intended for human consumption after softening or desalinization processes.

In all these regulations, chlorinated compounds are considered as cumulative parameters and the corresponding MAC ( $30 \mu\text{g l}^{-1}$ ) refers to their summation, despite the different toxicities and health effects of the individual compounds (Table 2). In addition, the present regulations do not allow for disinfection by-products such as

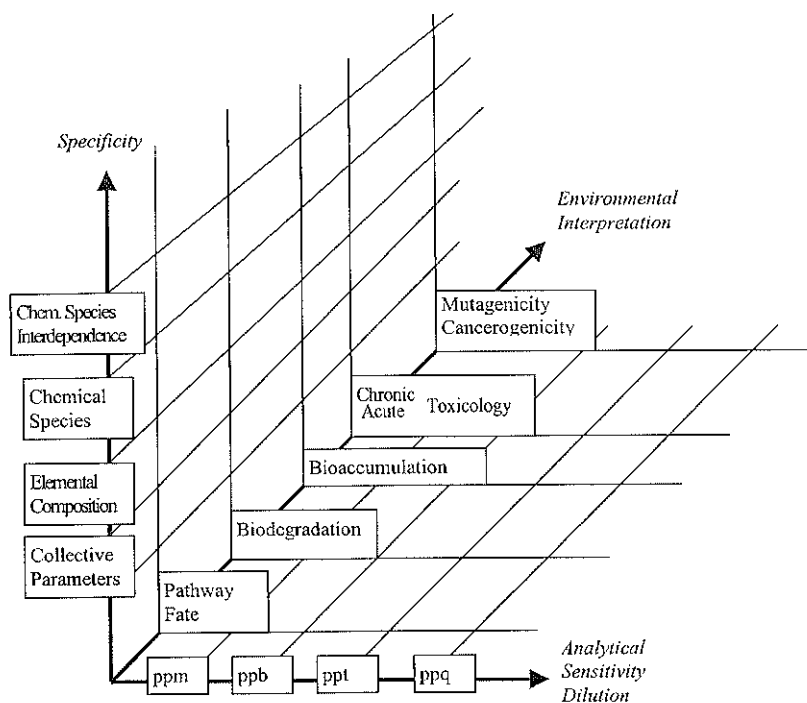


Fig. 1 Relationship between analytical sensitivity, specificity and environmental interpretation.

Table 2 Acute toxicology of chlorinated compounds ( $\text{mg kg}^{-1}$  body weight).

Substance	Oral $LD_{50}$ , rat	Oral $LD_{50}$ , rabbit	Oral $LDL_0$ , rabbit
Dichloromethane	167		1 900
Carbon tetrachloride	2 800	6 380	
Trichloroethylene	2 402	7 330	
Tetrachloroethylene	8 850	5 000	
1,1,1-trichloroethane	10 300	5 660	
1,1,2- trichloroethane	1 140		
Chloroform	800		500
Bromodichloroethane	916		
Chlorodibromoethane	840		

trihalomethanes (THMs) and haloacetic acids (HAAs), which are considered to be the same in terms of toxicity and health effects as any other halogenated compounds.

## A PROPOSAL TO MODIFY THE EEC DIRECTIVE AND WHO GUIDELINE

In 1993, WHO published the first volume of the new Guidelines for Drinking Water Quality concerning microbiological agents, chemicals, and radionuclides.

For chemicals, WHO guidelines follow two different kinds of procedures for substances that show or do not show a toxic threshold; the concept of threshold implies that there is a dose below which it is reasonable to assume that no toxic effects will

occur. The biological effects of a chemical depend on the concentration of the parent compound or its metabolites in target organs or tissues.

Concentration is, in turn, a function of absorption, distribution, metabolism and excretion; therefore only a fraction of the ingested dose reaches the site of its biological action. It may be that biological action takes place only when an effective concentration is reached.

Epidemiology is the only direct way to determine whether a substance produces toxic effects in humans. However, there are only a few epidemiological studies dealing with exposure to environmental contaminants through drinking water. Few studies deal with new chemicals of concern.

When available, epidemiological surveys have limitations. The main limitation is that the low concentrations generally found in water make it difficult to detect statistically significant increases in the pathologies caused (which occur after long exposure) and to separate out confounding factors. As a consequence, testing on animals and extrapolation to humans is the main method for determining MACs. Toxicological studies are therefore carried out to determine the highest dose at which no significant effect can be observed (i.e. No Observed Effect Level, NOEL). Starting from this value, it is possible to define the Acceptable or Tolerable Daily Intake (ADI or TDI) after applying an uncertainty factor, generally in the range of between 100 and 1000. From the ADI or TDI, the acceptable intake due only to water consumption can be calculated and thereafter the guideline can be determined considering an average water consumption of  $2 \text{ l d}^{-1}$ , a body weight of 70 kg and a lifetime (70 years) exposure.

Halogenated solvents belong to parameter 32 (i.e. halogenated compounds that do not belong to parameter 55) of DPR no. 236, whose MAC is  $30 \mu\text{g l}^{-1}$ ; guide values proposed by WHO vary from  $1 \mu\text{g l}^{-1}$  for trichloroacetonitrile to  $2000 \mu\text{g l}^{-1}$  for 1,1,1-trichloroethane.

Besides parametric limits fixed by guidelines WHO has defined a cumulative guide value for four trihalomethanes (THM) which are normally present in chlorinated water:

$$\frac{C_{\text{BROMOFORM}}}{GV_{\text{BROMOFORM}}} + \frac{C_{\text{DBCM}}}{GV_{\text{DBCM}}} + \frac{C_{\text{DCBM}}}{GV_{\text{DCBM}}} + \frac{C_{\text{CHLORONORM}}}{GV_{\text{CHLORONORM}}} \leq 1$$

The concentrations of these compounds in water seldom reach significant values in relation to chronic or acute toxicity. In the case of carcinogenic effects, it is necessary to evaluate the additional population risk of tumour development (additional tumours in a population of 10 000 people after 70 years exposure).

In these situations, the MACs obtained by means of mathematical models are low and frequently of the same order of magnitude as the concentration found in water.

## COMPARING LIMITS

Table 3 shows the carcinogenesis classes of some chlorinated compounds frequently found in Lombardy groundwater, and for comparison, the concentrations for which the US EPA estimates a cancer risk of 1/10 000, and guideline values proposed by WHO. Table 4 shows the limits in effect in some countries, and finally Table 5 shows the

**Table 3** Carcinogenicity of various compounds.

Substance	Carcinogenesis class			Conc. for $10^{-5}$ risk ( $\mu\text{g l}^{-1}$ )	WHO guide value ( $\mu\text{g l}^{-1}$ )
	CCTN	IARC	EPA		
<b>Halogenated compounds</b>					
Vinyl chloride	1	1	A	0.15	0.5
1,2 dichloroethane	2	2B	B2	4	30
1,2- dichloroethylene	3	3	C		30
Dichloromethane	2	2B	B2	50	20
Trichloroethylene	2	3	B2	30	70
Tetrachloroethylene	3	2B	B2	7	40
Carbon tetrachloride	2	2B	B2	3	2
1,1,1-trichloromethane	4	3	D		2000 (provisional)
1,1,2-trichloromethane	3	3	C		2000 (provisional)
2,4,6-trichlorophenol	2	2B	B2	30	200
<b>Halogenated disinfection by-products</b>					
Trichlorobromomethane	2	2B	B2	60	200
Chloroform	2	2B	B2	60	200
Dichlorobromomethane	–	2B	B2	6	60
Dibromochloromethane	–	3	C	4	100
Tribromomethane	–	3	B2		100

**Table 4** MACs by country.

Substance	France	UK	Germany	Norway	USA	Canada	WHO	EEC
Dichloromethane	30				100		20	20
Trichloroethylene	30	30	25 (30)	<5	5	5	70	40
Tetrachloroethylene	10	10	25 (10)	<10	5	50	40	40
Chloroform	30				100		200*	40 <sup>†</sup>
Carbon tetrachloride	3	3	3		5	5	2	
Bromodichloromethane								15 <sup>†</sup>

\*As a DBP, for  $10^{-5}$  excess risk.

<sup>†</sup>The samples for these parameters are to be taken after any chlorine contact time and at the outlet of water treatment plant. Where necessary the parametric value of bromodichloromethane can be increased to  $25 \mu\text{g l}^{-1}$  provided that the parametric value for chloroform is reduced to  $30 \mu\text{g l}^{-1}$ .

**Table 5** MACs proposed by ISS.

Substance	$\mu\text{g l}^{-1}$
Dichloromethane	20
Trichloroethylene	30
Tetrachloroethylene	7
Chloroform	30
Carbon tetrachloride	2

limits proposed by a work team at the Istituto Superiore della Sanità (ISS), (Carrere, 1993). In most cases, the established or proposed values in various countries differ by no more than one order of magnitude, while in some cases (when there is concordance with respect to the severity of toxicity and carcinogenesis) values are similar. For example, the MAC for chloroform is  $30 \mu\text{g l}^{-1}$  in France, and the WHO guideline value is  $200 \mu\text{g l}^{-1}$  (for disinfected water only).

## ANALYTICAL RESULTS

The presence of chlorinated solvents in the watershed of the Province of Varese, northwest of Lombardy, has been recognized since the early 1980s. The spatial distribution of the pollutants has remained about the same over time and is shown in Fig. 2 for 1996. The highest concentrations of solvents are located in the southern part of the Province of Varese, which is an industrialized densely populated area, while the northern part is less densely populated and industrialized.

The large amount of analytical data collected during the years 1991–1997 enables us to evaluate the suitability of the current MAC set by the Italian regulations to protect health. The MAC has resulted in additional costs for the community without lowering the risks to public health.

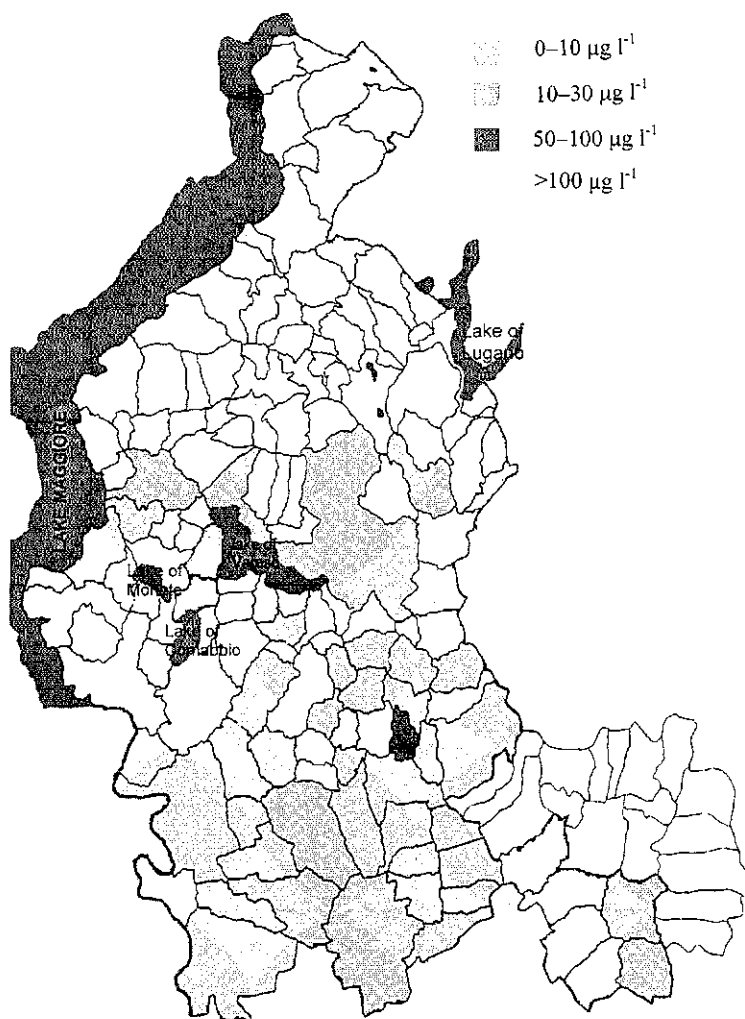


Fig. 2 Halogenated solvent distribution in the Province of Varese.

Table 6 shows the frequencies of occurrence of various concentrations of halogenated solvents measured in the wells of the Province of Varese in the years 1991–1997. Table 7 shows the concentration distribution of dichloromethane: concentrations in 0.2% of the examined samples exceeded the proposed MAC. For tetrachloroethylene (Table 8), 95.7% of samples were at or below  $40 \mu\text{g l}^{-1}$ , while 94.3 % of the samples were lower than or equal to  $30 \mu\text{g l}^{-1}$ . The situation would significantly change if the proposal of the Istituto Superiore della Sanità for a limit at  $7 \mu\text{g l}^{-1}$  were accepted (80.4% of the samples would comply with the MAC). For carbon tetrachloride (Table 9), 1.2% of the samples would exceed the MAC.

**Table 6** Halogenated solvents total concentration distribution.

Concentration ( $\mu\text{g l}^{-1}$ )	Frequency	Percent	Cumulative percent
= 10	4123	58.3	58.3
11–20	1030	14.6	72.9
21–30	601	8.5	81.4
31–50	630	8.9	90.3
51–100	360	5.1	95.4
101–200	142	2.0	97.4
201–500	82	1.2	98.6
> 500	100	1.4	100.0

**Table 7** Dichloromethane concentration distribution.

Concentration ( $\mu\text{g l}^{-1}$ )	Frequency	Percent	Cumulative percent
= 20	6422	98.8	99.8
21–50	7	0.1	99.9
51–100	4	0.1	100.0

**Table 8** Tetrachloroethylene concentration distribution.

Concentration ( $\mu\text{g l}^{-1}$ )	Frequency	Percent	Cumulative percent
= 10	5685	80.4	80.4
7–30	982	13.9	94.3
31–40	96	1.4	95.7
41–50	37	0.5	96.2
51–100	88	1.2	97.5
101–200	61	0.9	98.3
201–500	70	1.0	99.3
> 500	49	0.7	100.0

**Table 9** Carbon tetrachloride concentration distribution.

Concentration ( $\mu\text{g l}^{-1}$ )	Frequency	Percent	Cumulative percent
= 0.5	6808	96.3	96.3
0.5–1.0	76	1.1	97.4
1.0–1.5	38	0.5	97.9
1.5–2.0	28	0.4	98.3
2.0–3.0	34	0.5	98.8
> 3.0	84	1.2	100.0

## CONCLUSIONS

It should be noted that in many cases, the water in Lombardy is polluted by several solvents. It is therefore important to consider the sum of the chlorinated compounds, or of any other class of compounds. While it is necessary to adopt defined limits for each compound to prevent undue exposure to highly carcinogenic agents, it is also important to introduce a corrective factor to account for possible synergistic effects. Applying criteria similar to that proposed by WHO for disinfection by-products:

$$\sum \frac{C_i}{GV} \leq 1$$

where:  $C_i$  = concentration of  $i$ th compound and  $GV$  = guide value for  $i$ th compound.

In defining new MACs, it is also necessary to consider exposure pathways besides ingestion. According to Little (1992) and McKone (1987), inhalation exposure during a shower, or using a dishwasher or washing machine could be significant. The estimated inhaled quantity varies: McKone (1987) calculated that the indoor inhalation exposure due to the use of polluted water is six times the exposure attributable to the consumption of 2 l d<sup>-1</sup> of the same tap water. Assuming a breathing rate of 20 m<sup>3</sup> day<sup>-1</sup>, Little (1992) concluded that a single ten minute shower is equivalent to approximately 1.5 times the exposure received by drinking 2 l of the same water.

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