

Status report on aquatic micropollution in french inland waters

J. GARRIC

*Cemagref, Laboratoire d'écotoxicologie, UR Biologie des Ecosystèmes Aquatiques, 3 bis Quai Chauveau, F-69 336 Lyon Cedex 09
e-mail : jeanne.garric@cemagref.fr*

SUMMARY

The freshwater toxic pollution is monitored from 1990, as a part a part of the French Watershed Network, implemented and managed by the DIREN and the Water Agencies.

To illustrate the freshwater toxic pollution, chemical data analysed (1995-1999) in two industrial and urban French watersheds are discussed and compared to available quality criteria in water and sediment. Herbicides are the main pesticides detected in freshwater, and PAHs, PCBs and metals are always measured in sediment, sometimes at high concentrations. Very few data on the biota contamination are available and efforts are necessary to improve the data quality.

KEY-WORDS : freshwater - sediment - fish - contamination - metals - organic compounds - monitoring network

RÉSUMÉ

La contamination des eaux douces par les micropolluants : quelques données françaises. Par J. GARRIC.

La pollution des eaux douces (eaux de surface et sédiment) par les micropolluants organiques et métalliques est surveillée depuis 1990 dans le cadre du réseau national de bassin, par les DIREN et les Agences de l'eau. Ces données sont disponibles auprès du réseau national des données sur l'eau et des agences de l'eau.

Les données de micropollution (1995-1999, eau, sédiment, poissons) de deux grands bassins urbains et industriels sont analysées pour illustrer les niveaux de contamination des milieux aquatiques, en regard des seuils de concentrations proposés dans le cadre du Système d'Evaluation de la Qualité des Agences de l'eau (SEQ-eau), et de valeurs récemment publiées au niveau international.

Les herbicides apparaissent comme les principaux pesticides détectés dans les eaux de surfaces, alors que les HAPs, les PCBs et les métaux sont systématiquement présents dans les sédiments à des concentrations parfois suspectes d'effet toxique. Les lacunes les plus importantes concernent les données sur la contamination des organismes, pour lesquelles des efforts d'acquisition, de standardisation et d'interprétation sont indispensables.

MOTS-CLÉS : eau douce - contamination - sédiment - poisson - métaux - polluants organiques - réseau de surveillance.

1. Introduction : the micropollutants monitoring network in the french freshwaters

The freshwater quality monitoring is managed by the French ministry of the Environment and 6 water agencies since 1971. First it dealt with organic pollution and nutrients (nitrogen compounds, phosphorus...).

More recently, in agreement with the European directives, a national network has been implemented dealing with the micropollution. A first monitoring program started in 1991.

This monitoring program is a part of the French Watershed Network, implemented and managed by the DIREN (Regional Office of the Environment) and the Water Agencies. This network aims to check the long term water quality, to prevent pollution and to manage the river restoration, and at last to inform the water users.

Based on the results of the first monitoring program (91-96) several recommendations were proposed to improve the 1997-2001 program that led to :

- a better selection of the sampling sites, based on the knowledge of the toxic sources,

- an extension of the control towards the upstream zones of the watersheds,
- an improved selection of the analysed compounds, based on their occurrence and their toxicity and ecotoxicity levels,
- an homogenisation of the sampling and analysing protocols.

2) The monitoring protocol

1) ANALYSED SUBSTANCES

Numerous substances are analysed, depending on the substrate.

A main list of micropollutants was defined, which are checked on all the stations. This list includes 31 pollutants from urban and industrial sources and 7 from agricultural sources [1]. The table I presents the chemical analysed and the sampled substrates. Several of these substances was recently identified as priority hazardous substances by the European commission [2].

In addition to this main list, a complementary list of compounds of interest is proposed, based on different european or american lists (European directive 76/464, US EPA,

Canada, international commission for the Rhine protection). Depending on the local situation several compounds may be analysed from this list.

For example, additionally to the main list, at least 228 pesticides and 47 others organic compounds are routinely analysed in the Rhône Méditerranée Corse watershed, respectively in water and sediment (95-99).

2) ANALYSED SAMPLES AND SAMPLING FREQUENCY

The micropollutants are checked in water, sediment, bryophytes and /or suspended matter, according with their physico-chemical properties. One or more matrix may be analysed.

Water is analysed without filtration. Several problems are encountered when water is used for the control : the samples representativeness, the very low concentrations in water ($\mu\text{g/l}$, ng/l).

Sediment and *suspended matter (SM)* are analysed to measure the concentrations of the metals and substances with low hydro solubility ($\log K_{ow} > 3$, high K_{oc}). Sediment are considered as a sink for the contaminants, and more representative of the ecosystem contamination than water. But the concen-

Compounds	Industrial source	Agricultural source	Substrate	EC priority
Metals total	Arsenic, chrome, copper, nickel, lead, zinc		water, bryophyte, sm, sediment	
	cadmium, mercury			*
Compounds	Industrial source	Agricultural source	Substrate	EC priority
PAHs	Benzo(a)pyrene, benzo(b)fluoranthene, benzo (g,h,i)perylene, benzo(k)fluoranthene, fluoranthene, indeno(1,2,3)cd pyrene anthracene, benzo (a)anthracene, di benzo (ah)anthracene, methyl(1)fluoranthene, methyl (2)naphtalene, phenanthrene		sm, and sediment	*
halogenated aromatic chlorinated aliphatic	Hexaclorobenzene PCBs (28,52,101,118,138,153,180) Tetrachloroethylene, trichloro ethane (1,1,1), trichloroethylene		sm, and sediment water	*
organochlorinated pesticides		lindane	water, sm, sediment	
Herbicides		Aminotriazole, atrazine, desethylatrazine, diuron, simazine, trifluraline	water, sm, sediment	

Sm : suspended matter ; EC : European community

TABLE I. — Common list of analysed micropollutants.
TABLEAU I. — Liste des micropolluants et des matrices analysés.

trations can be highly variable at the same station. Only fine grained (< 2 mm) recent deposit are sampled and analysed once a year.

Briophytes are used as bioindicators of the contamination by metals. In effect, these aquatic plants can concentrate micropollutants from the water. They are sampled once a year and analysed to measure bioavailable metals concentrations.

Biota. Analysis on biological samples are not routinely performed. Few data are available from monitoring studies. Fish are the main species used to assess the level of the biota contamination.

3. Contamination levels

To illustrate the inland freshwater micropollution and the levels of contamination we analyse some data available from two monitoring networks. These watersheds present large urban areas and important agricultural and industrial activities. When possible, we compare the measured concentra-

tions with the concentrations proposed at the moment as quality criteria for water and sediment. These criteria are all based on biological effect (sublethal and lethal).

For contaminants in freshwater, we used toxicity thresholds proposed by the French freshwater quality evaluation system (SEQ- eau) [3]. From these thresholds five quality classes are defined (high, good, acceptable, bad, very bad). For sediment we compare the chemicals concentrations with the two threshold effect levels proposed by Mc DONALD *et al.*, 2000 [4], the Threshold Effect Concentration (below the TEC very low probability of toxicity is expected) and the Probable Effect Concentration (above PEC high probability of toxicity is expected).

1) FRESHWATER POLLUTION

From data used, table II presents some of the more frequently (> 10 times) organic compounds detected in freshwater. There are mainly industrial chlorinated solvents, with concentrations below the thresholds 1 or 2 of SEQ eau, which correspond to an high or good water quality.

Table III shows levels of freshwater metal contamination. These values are compared with the probable sublethal toxi-

	N data	N detected	%	Concentration level
chloroforme	475	469	99	<T2 (120µg/l)
dichlorobenzène-1,2	317	303	96	<T2 (200µg/l)
dichlorobenzène-1,4	267	253	95	<T1 (20µg/l)
hexachlorobenzène	80	49	61	T3<80%>T2 (0.07-7 µg/l)
tétrachlorure de carbone	475	251	53	?
trichloroéthane-1,1,1	281	82	29	<T1 (130 µg/l)
trichloroéthylène	281	12	4	<T1 (20 µg/l)
dichloroéthane-1,2	281	11	4	<T1 (1100 µg/l)

T1, T2, threshold concentration from SEQ-EAU

TABLE II. — Frequently organic micropollutants detected in water.

TABLEAU II. — Micropolluants organiques fréquemment détectés dans l'eau.

µg/l	average	mediane	min	max	T2	% samples >T2
Arsenic (49)	0.27	1	0.2	3.4	100	0
Cadmium (10)	0.85	0.2	0.1	0.6	0.37	40
Chrome (31)	2.15	2.0	1.0	6.3	18	0
Copper (62)	8.9	4.5	1.0	103	10	17
Mercury(17)	0.72	0.4	0.1	2	0.7	12
Nickel (39)	2.65	1.7	0.5	18.9	62	0
Lead (30)	2.14	2.0	1.0	8.1	52	0
Zinc (62)	48.9	29.5	1.0	480	43	0

Watershed 2 (number of available data)

TABLE III. — Examples of freshwater metal concentrations encountered in an industrial watershed.

TABLEAU III. — Concentrations métalliques mesurées dans l'eau d'un bassin industriel.

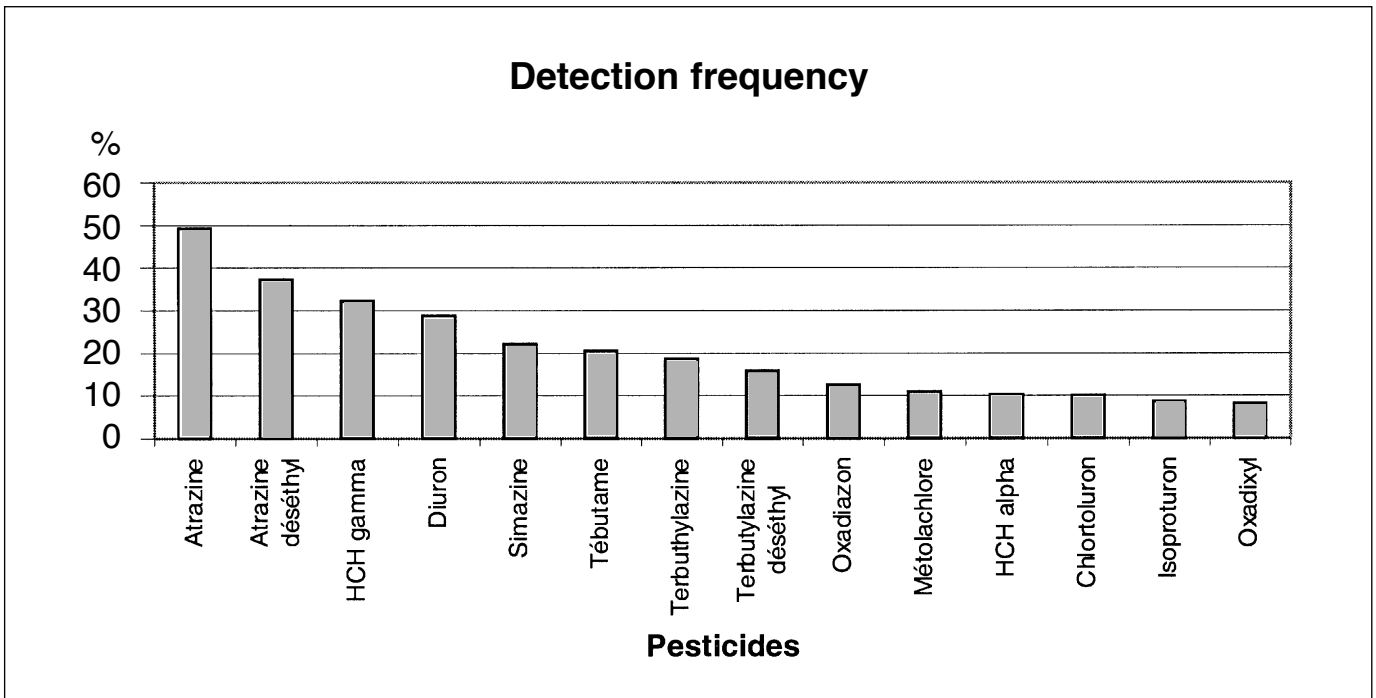


FIGURE 1. — Main pesticides measured in the watershed surface water.

FIGURE 1. — Principaux pesticides mesurés dans l'eau de surface.

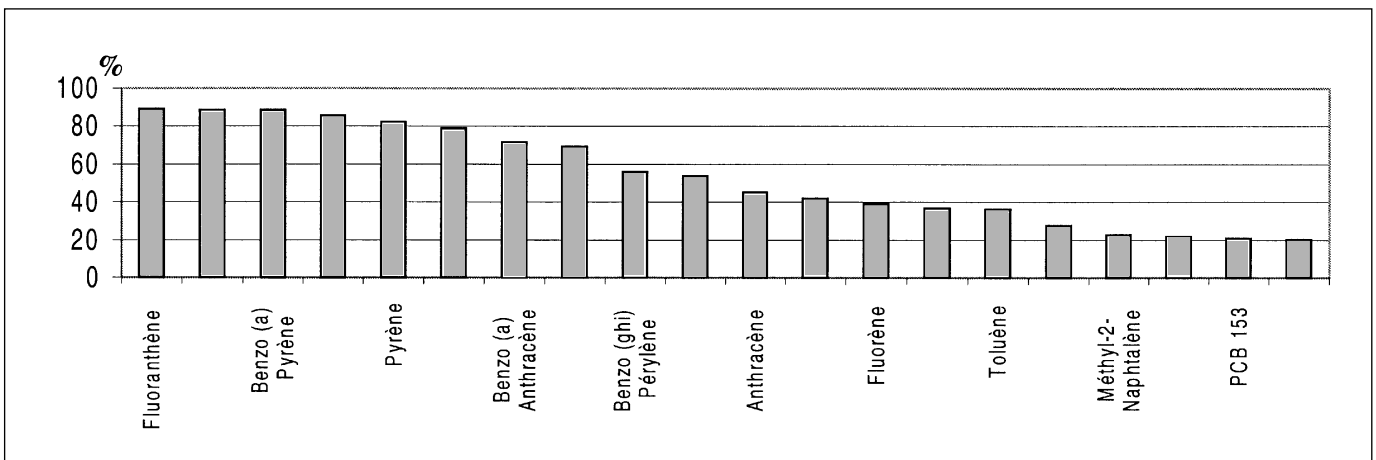


FIGURE 2. — Frequency of the sediment contamination by organic micropollutants (N = 454).

FIGURE 2. — Fréquence de contamination des sédiments par les micropolluants organiques.

city level (T2) (For an hardness between 50-200mg/l CaCO₃) proposed in the SEQ-eau.

In several cases sublethal and long term biological effects can be suspected for the aquatic species, with significant frequency.

2) PESTICIDES

From 235 compounds checked in freshwater, only 64 are detected above the detection limit in the watershed during the studied period (95-99). The more frequently detected com-

pounds are showed Figure 1. Except for the lindane, the herbicides are the main compounds significantly measured in the surface waters.

Based on the proposed threshold concentrations, the range of the concentrations is mainly include between thresholds 1 and 2 (Table IV)..

Same results have been showed by IFEN [5] from national dataset (1997-1998). Atrazine was quantified in more 58 % of 1047 sampling stations, and 73 % of the sampled stations (total 247) were qualified at least with a good quality label.

	Concentrations distribution
Chlortoluron	100% < T1
Atrazine	92% < T1, T2 < 7% < T1
Diuron	T1 < 40%, T1 < 37% < T2, 3% > T2
Lindane	T1 < 100% T2
Simazine	T1 < 83% < T2, 100% < T3
Isoproturon	70% < T1, T1 < 30% < T2

T1, 2 : threshold concentrations

TABLE IV. — Concentration distribution for some frequently detected pesticides.

TABLE IV. — Distribution de concentrations pour quelques pesticides fréquemment détectés.

4. Sediment contamination

In sediment PAHs and PCBs are the main organic compounds detected. Metals are always presents too. Figure 2 shows the more frequently organic compounds detected in the sediment (> 20 times) from our dataset.

PAHs are measured in 90 % of the sediment sampled. Based on TEC and PEC values for total PAHs, PAHs concentrations are probably not toxic for 68 % of the samples, 3 % are probably toxic, but 29 % cannot be qualified and require further investigations, as bioassays to assess their biological quality.

Sediment are also frequently contaminated by PCBs congeners (24 % of the samples). For 54 % of the samples,

PCBs concentrations are less than TEC, but 43 % are include between TEC and PEC.

1) METALS

Fine sediment are widely contaminated by metals. Here we give examples of contamination levels from two watershed networks (Table V). We compare again the measured concentrations with the sediment quality criteria (PEC) and calculate the percentage of samples with concentrations above the probable toxic threshold.

According with the watershed, sediment contamination by metals can be high. Moreover, a significant number of the sampled sediment are likely to cause toxic effect on the benthic organisms.

Mg/kg	average	mediane	min	max	PEC	% >PEC
Arsenic	14,6	9	0,5	540	33	7
Cadmium	1,2	0,8	0,01	49	4,98	3
Chrome	42,72	38	2,4	430	111	2
Copper	36,92	21	1,4	740	149	2
Mercury	0,192	0,08	0,005	2,52	1,06	3
Nickel	24,122	21,5	1,5	130	48,6	5
Lead	39,81	27	0,5	690	128	3
Zinc	130,13	82	9,0	1990	459	2

Watershed 1 : 455 analysed samples

TABLE V. — Contamination of sediment by metals.

TABLEAU V. — Contamination métallique des sédiments.

Mg/kg	average	mediane	min	max	S2	% >PEC
Arsenc	19.6	7.8	0.2	189	33	17
Cadmium	0.85	0.65	0.13	3	4.98	0
Chrome	111	53.4	7.8	449	111	26
Copper	71.3	41.2	6.5	391	149	4
Mercury	2.3	0.55	0.02	30.2	1.06	30
Nickel	41.5	33.8	8.1	99.5	48.6	14
Lead	149.8	76.9	17.3	1367	128	28
Zinc	294.1	245.5	44.3	1306	459	12

Watershed 2 : 120 analysed samples

TABLE V (continuing). — Contamination of sediment by metals.

TABLEAU V (suite). — Contamination métallique des sédiments.

2) PESTICIDES

Few pesticides are detected in sediment. From our data set only 20 compounds are measured, from 176 analysed. There are mainly chlorinated pesticides, generally no more used, but with an high persistency, and high adsorption capacity on soil or sediment (Fig. 3).

3) BIOTA CONTAMINATION

It does not exist national monitoring network, dealing with the freshwater fish contamination, probably due to the fact that human consumption of freshwater fish is not so important in France.

Nevertheless, some monitoring studies exist (Mainly managed by the French hydrobiological and fish network,

within the scope of fish communities status monitoring), but these studies are carried out with different protocols and dealt with different compounds and species. More, the organs of several fish are generally pooled to perform the analysis. So, from these rare data it is not possible to have an overview of the fish contamination in the different French watershed, nor to easily study relationships between freshwater (water, sediment, suspended matter) and fish contamination.

To give an idea of the fish contamination levels encountered in some industrial areas, we present some results from two different studies carried out on industrial watersheds. Only results on fish muscles are considered here. They are compared with the available contamination thresholds for human consumption [7], and for freshwater species protection [8] (Table VI).

Detection frequency

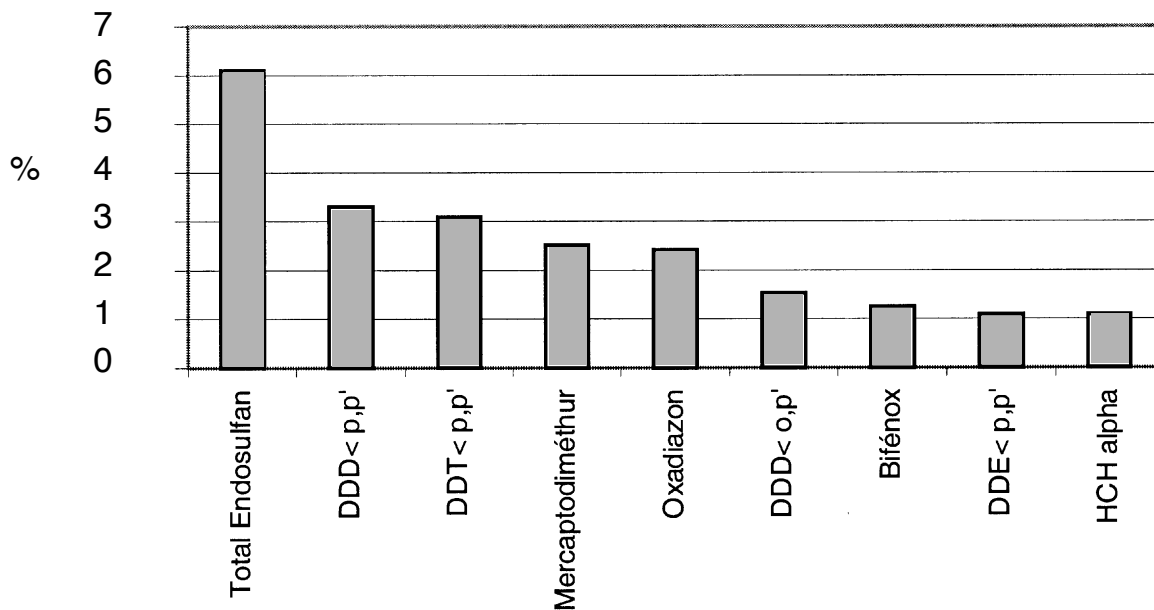


FIGURE 3. — Pesticides detected in sediment.
 FIGURE 3. — Pesticides détectés dans les sédiments.

	As	Cr	Cd	Cu	Hg	Ni	Pb	Zn
Roach	<0.1-0.17	0.05-0.44	<0.01-0.02	0.17-1.25	<0.01-0.30	<0.09-0.17	<0.05-0.16	2.97-38.8
Anguilla	<0.1-0.49	0.06-0.27	<0.01-0.04	0.19-0.89	0.03-0.67	0.13-0.29	0.07-0.27	6.25-34.96

From Noppe et Prygiel, 1999 [7]
 Exceed human consumption threshold, Exceed species protection threshold

TABLE VI. — Contamination of fish sampled in some rivers of the watershed Artois Picardie (55 stations).

TABLEAU VI. — Contamination des poissons prélevés dans des cours d'eau du bassin Artois Picardie.

Compared to some reference values measured in the watershed, mercury is the main contaminant in some areas. Anguilla are frequently the most contaminated species (NOPPE and PRYGIEL 1999), probably due to their high lipids content. But, in this study none metals exceed the authorised values for the human consumption, whereas the threshold values for the aquatic species protection can be exceeded in some cases (Hg, Zn).

Additional results are available on fish sampled in the Saône and Rhône rivers in 1995-96. (Table VII).

Organochlorine compounds and metals are present in fish muscles. Authorised values are exceeded in rare cases for lead and pp'DDE, and some individual PCBs congeners (mainly PCB 153), but not for total PCBs. Carnivorous fish do not seem more contaminated than omnivorous fish (chub, *Leuciscus cephalus*). In this case too, threshold values for the aquatic species protection are exceeded for metals and organic compounds.

In these examples, fish contamination is frequently below the thresholds of human consumption. PCBs congeners and mercury are the main compounds which cause some problems. But, considering the aquatic species protection, the quality thresholds are more often exceeded.

Nevertheless, few data are available dealing with the chemical contamination of fish in reference areas, and with the long term hazard in field populations. So, to improve our knowledge about the causes, the persistence, and the consequences on fish populations of the chemical contamination, it is essential to carry out long term monitoring programs, with selected species and standardised protocol of sampling and analysis.

5. Conclusions

From the monitoring networks, large datasets are now available to give an overview of the chemical contamination of the freshwater ecosystems, even if additional efforts can certainly still be made to improve their interpretation (detection level, confidence interval...). Nevertheless these data

only concern some compounds or families, as metals, organochlorines (pesticides, PCBs...) PAHs or detergents.

Information about the freshwater ecosystems contamination by others widely used chemicals, likely to be significantly discharged in freshwater as pharmaceuticals, veterinary or personal care products, are not yet available.

In addition, considering the various harmful effects that the persistent organic compounds may cause (accumulation in food chain, reproductive effect, carcinogenicity...) JONES and DE VOOGT [9] also highlight the need to shift from detailed studies on the more traditional POPs (PCBs, PCDDs, PAHs) to metabolites and new classes of these products (PBDE, chlorinated paraffins, toxaphene) and perhaps more polar persistence compounds as some chlorinated phenols.

Whatever, simultaneously with the relevant (hazardous and widely occurring) contaminants which must be checked to protect freshwater ecosystems, efforts must be carried out :

- to improve the freshwater ecosystem quality criteria dealing with the well known micropollutants (in water, sediment and biota), considering the bioavailability of the compounds, the possible metabolites and the effects of the mixtures
- to develop and routinely use relevant biological endpoints (i.e. biochemical or physiological biomarkers), likely to detect unexpected hazardous contaminants.

Acknowledgements

S. LARONDE Office International de l'Eau, D. FARINA Office International de l'Eau, M. BONNEFILLE, agence de l'eau Rhône Méditerranée Corse, F. SOLACROUP, Agence de l'eau Adour Garonne, J. PRYGIEL, Agence de l'eau Artois Picardie.

Some of the useful web sites dealing with the french freshwater ecosystems quality...

<http://www.rnde.tm.fr>

<http://rdb.eaurmc.fr>

Mg/kg/ww	Cd	Hg	Pb	Zn	PCB tot	pp'DDE	Hexachloro benzene	Gamma HCH	Alpha HCH
Carnivorous fish	<0.01- <0.2	<0.02- 0.9	<0.01 <0.2	6.1- 10.2	<0.010- 0.418	<0.005- 0.025	<0.001-0.007	0.001- 0.014	<0.001- 0.014
Chubs	<0.01- <0.2	0.1-0.7	<0.01- 0.6	4.4- 14.4	<0.01- 0.590	<0.05- 0.165	<0.001-0.008	0.001- 0.019	<0.001- 0.012

(Data from LDA 39 [7])

Exceed human consumption threshold, Exceed species protection threshold

TABLE VII. — Contamination level by some metals and organic pollutants of fish (muscles) from Saône and Rhône rivers.

TABLEAU VII. — Contamination organique et métallique de poissons du Rhône et de la Saône.

References

1. — La mesure des micropolluants dans le cadre du réseau national de bassin. Méthodologies et recommandations. Étude Inter agence n° 53, 1997.
2. — Commission des communautés européennes. 2000/0035(COD). Décision du parlement européen et du conseil établissant la liste des substances prioritaires dans le domaine de l'eau (proposition modifiée, 16/01/00).
3. — Système d'Évaluation de la Qualité des cours d'eau. Annexe A grille de seuils par altération. Étude Inter agence n° 64, 1999.
4. — MacDONALD D.D., INGERSOLL C.G. and Berger T.A. : Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 2000, **39**, 20-31.
5. — IFEN : Les pesticides dans les eaux, 2000, Bilan 1997-1998.
6. — GIRARD P. : Contamination des poissons par les micropolluants organiques et métalliques, 1999. Réseau National de Bassin Adour Garonne. Exploitation de la campagne de mesures 1998. Agence de l'Eau Adour Garonne, Février 1999.
7. — NOPPE K. and PRYGIEL J. : Contamination métallique des poissons du bassin Artois Picardie. Aide à l'interprétation des résultats à l'usage du gestionnaire. *Bull. soc. zool. Fr*, 1999, **124**, p. 397-409.
8. — La qualité des poissons de la Saône et du Rhône. État sanitaire et hygiénique. Campagne 1995-1996. Agebe de l'eau RMC. DIREN Rhône Alpes. Laboratoire Départemental d'Analyses du Jura.
9. — JONES K.C. and P. DE VOOGT. : Persistent organic pollutants (POPs) : state of science. *Environmental pollution*, 1999, **100**, p. 209-221.