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The role of sediments in the assessment of ecological quality of European river bodies

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Summary. - Member States of the EU are presently involved in the enforcement of the Directive of the Council and European Parliament 2000/60/CE, the so-called Water Framework Directive (WFD), establishing a frame for the common water policy of the Union. A major objective of the WFD is to reach within 2015 a good ecological status for all relevant surface water bodies of the Union territory. The assessment of the ecological status must be supported by the assessment of both the hydromorphological conditions of the water and its chemical status as represented by basic chemical parameters such as temperature, pH, oxygen balance and nutrients, and the presence or absence (*vs* environmental quality standards or natural background concentration) of specific synthetic and non-synthetic micropollutants. According to this approach, the assessment of the presence in any phase (water, sediments and biota) constituting the water body of micropollutants at concentrations below the environmental standards will guarantee the protection from toxic and ecotoxic effects on humans, animal and vegetal communities associated with the water body. In this context, the state of the art in Italy as compared to that in some non-EU states, particularly in Armenia, is discussed.
Key words: micropopollutants, sediments, ecotoxicology, water body, quality.

Riassunto *(Il ruolo dei sedimenti nella valutazione dello stato ecologico dei corsi d'acqua in Europa).* - Gli Stati Membri della UE sono attualmente impegnati nell'attuazione della Direttiva del Consiglio e del Parlamento Europeo 2000/60/CE (*Water Framework Directive,* WFD) che definisce i criteri e gli obiettivi della politica comune sulle acque. L'obiettivo principale è il conseguimento entro il 2015 di un buono stato ecologico per tutti i corpi idrici significativi. La determinazione dello stato ecologico è sostenuta dalle condizioni idromorfologiche e chimiche dei corpi idrici derivanti dal livello di parametri chimico-fisici di base quali la temperatura, il pH, il bilancio dell'ossigeno ed i nutrienti, e dalla presenza/assenza (in confronto agli standard di qualità ambientali o al livello di fondo naturale) dei microinquinanti sintetici e non. In base a questa impostazione la determinazione della presenza in ognuna delle fasi che costituiscono il corpo idrico (acqua, sedimenti e biota) dei microinquinanti ad una concentrazione inferiore allo standard di qualità ambientale consente di garantire la protezione dell'uomo, degli animali e dei vegetali delle comunità associate al corpo idrico da effetti tossici ed ecotossici. A fronte di questi aspetti della tutela delle acque viene discusso lo stato dell'arte in Italia in confronto a quanto avviene in altri Stati esterni alla Unione Europea.
Parole chiave: microinquinanti, sedimenti, ecotossicologia, corpi idrici, qualità.

International framework

The Global Report of the United Nations (22 May 2002) "UNEP's Third Global Environment Outlook (GEO-3) [1] warns world population that 70% of all nature is significantly stressed and endangered. The global cost due to sea pollution, both in the sense of a strictly economical, but also related to human health, damage is estimated approximately in 13 billion dollars/year. All climatic changes, streams of oils, organic emissions and dust, plums of sewage, heavy metals and sediments are adversely affecting the oceans.

As regards the state of the aquatic environment in Europe [1] freshwater stocks are unevenly distributed, with parts of Southern, Western and South-Eastern Europe being noticeably water stressed. The health of coastal and marine areas has worsened, particularly in Southern and Western Europe and on the Mediterranean coastline. Geographically, there has been an amelioration of some environmental problems in Western Europe and general (but far from universal) deterioration in Central and Eastern Europe, with recent signs of a significant recovery in many countries. The development of strong environmental policies in the European Union stands for continued progress in this area.

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Member States of the EU are presently involved in the enforcement of the Directive of the Council and European Parliament 2000/60/EC, the so-called Water Framework Directive (WFD) [2], establishing a frame for the common water policy of the Union. A major objective of the WFD is to reach within 2015 a good ecological status for all relevant surface water bodies of the Union territory. The achievement of this objective requires Member Sates to establish a monitoring network designed to provide a comprehensive and significant assessment of the ecological and chemical status of each water body pertaining to the categories of rivers, lakes and transitional and coastal waters inside a river basin area.

Good ecological status was defined as the condition when the value of the biological quality elements (phytoplacton, macrofites and phytobenthos, benthic macroinvertebrates, fish fauna) for a given water body differ slightly from those met in the absence of anthropic alteration in a reference site specific for the water type considered (high status, see Table 1). The assessment of the ecological status must be supported by the assessment of both the hydromorphological conditions of the water and its chemical status as represented by basic chemical parameters such as temperature, pH, oxygen balance and nutrients, and the presence or absence (*vs* environmental quality standards or natural background concentration) of specific synthetic and non-synthetic micropollutants.

Special attention should be paid to those conditions that make a water body at risk in the achievement of the environmental objective. For those water bodies specific operational monitoring programmes should be put in place to verify the effectiveness of the measures undertaken to reach the environmental objectives.

According to this approach, the assessment of the presence in any phase (water, sediments and biota) constituting the water body of micropollutants at concentrations below the environmental standards will guarantee the protection from toxic and ecotoxic effects on humans, animal and vegetal communities associated with the water body.

A comparison of the importance of the presence of micropollutants in sediments in two quite different geographical areas (the Mediterranean and the Caucasian areas) will show the general importance of this phenomenon to control the micropollutants impacts on water resources.

Priority pollutants in EU and Italian legislations

According to the definition of ecological status (Table 1), Environmental Quality Standards (EQSs) for water, sediments and biota in aquatic systems are needed to assess risk to the health of humans and other living species due to toxicity and ecotoxicity of the major micropollutants. From the point of view of characterisation of sediments, a major role can be ascribed to the development of selective analytical methods including the complete process from sampling to detection.

In the field of installations for handling substances dangerous to water bodies, an important role is also played by the EC Directive on the control of major disasters involving dangerous substances

Table 1. - Water Framework Directive general definition for the chemical contribution to a high, good ecological status including the micropollutants presence in rivers

Quality element value	High status	Good status	Moderate status
General chemical quality elements	Values correspond totally or nearly totally to undisturbed conditions Nutrient concentration, salinity, pH, oxygen balance, acid neutralising capacity within the range associated with undisturbed conditions	Temperature, oxygen balance, pH, acid neutralising capacity and salinity do not reach levels that affect the functioning of the type specific ecosystem	Conditions consistent with the achievement of the values expected for biological elements in that type specific ecosystems
Synthetic and natural micropollutants	Concentration near to zero or lower than the detection limits of the most advanced analytical techniques of general use	Concentration not in excess of EQ standard	Conditions consistent with the achievement of the values expected for biological elements in that type specific ecosystems

[3], the Construction Products Directive [4] and the standardization procedure under CEN (Comité Européen de Normalisation). The EU countries have common regulations governing the classification and labelling of chemical substances. They also carry out the joint classification and assessment of chemical substances.

The priority pollutants (PP) and the priority hazardous pollutants (PHP) for EU were selected according to the screening procedure common monitoring-based modelling-based priority scheme (COMMPS).

The priority substances have been identified in accordance with the Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community [5] and the Decision 2455/2001/EC [6] of the European Parliament and of the Council of 20 November 2001, establishing the list of priority substances in the field of water policy and amending WFD 2000/60/EC [2].

The actual criteria prescribed by the WFD are embedded in an overall concept of river basin planning which is underpinned by the physical structure of the river catchments areas and therefore extends beyond Member State boundaries. To implement these planning requirements there will thus be a need for closer cooperation between different administrative bodies and different countries.

Hence, the Decision no. 2455/2001/EC [6] ranks in order of priority the substances for which quality standards and emission control measures should be set at the Community level. In Annex X of this Decision the proposal has been made for a complete list of priority substances or groups of substances (including anthracene, benzene, cadmium and its compounds, tributyltin and naphthalene, see Table 2). The COMMPS approach has led to a first selection of 33 priority pollutants including 11 priority dangerous pollutants. These last micropollutants should be phased-out avoiding any emission, discharge and losses of these molecules within 2020. The Committee for the implementation of WFD will define through regulations pollutant EQSs and suggest the most advanced analytical methods (from sampling to detection) to be used in monitoring.

The safety factors, which set appropriate safety factors in each case consistent with the nature and quality of the available data and the guidance are given in section 3.3.1 of Part II of the "Technical guidance document in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment for existing substances" [7]. The procedure reported in Table 3 was used to select the PP and PHP. The EU Water WFD contains provisions that call for assessment of contaminated sediments. First, article 16(7) of the Directive states that the Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface water, sediments or biota. If quality criteria were to be defined for sediments, then monitoring would be required to establish compliance with such criteria. Secondly, it is clear from the WFD that sediment monitoring can play a role when assessing impacts on environmental quality.

In order to address these requirements of the WFD, the Working Group on Analysis and Monitoring of Priority Substances (AMPS) has considered the

Table 2. - Priority micropollutants according the COMMPS approach and the corresponding EQSs in Italian legislation for fresh water

Priority pollutants	EQS (µg/l) Fresh water Italian legislation
1. Alachlor	0.03
2. Benzene	0.2
3. Chlorfenvinphos	0.0002
4. 1,2-Dichloroethane	0.3
5. Dichloromethane	1
6. Fluoroanthene	0.01
7. Nickel and its compounds	1.3
8. Trichloromethane	1
9. Brominated diphenylethers	--
10. Cadmium and its compounds	0.1
11. C-chloroalkanes	0.5
12. Hexachlorobenzene	--
13. Hexachlorobutadiene	--
14. Hexachlorocyclohexane (gamma-isomer, lindane)	0.001
15. Mercury and its compounds	0.02
16. Nonylphenols [4-(para)-nonylphenol]	0.03
17. Pentachlorobenzene	0.003
18. Polyaromatic hydrocarbons (PAH) (benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene)	0.005 (total) 0.001 (single species)
19. Tributyltin compounds (tributyltin-cation)	0.0001
20. Anthracene	0.01
21. Atrazine	0.01
22. Chlorpyrifos	0.0001
23. Di(2-ethylhexyl)phthalate (DEHP)	0.3
24. Diuron	0.02
25. Endosulfan (Alpha-Endosulfan)	0.00001
26. Isoproturon	0.02
27 Lead and its compounds	0.4
28. Naphthalene	0.01
29. Octylphenol (para-tert. octyphenol)	0.01
31. Simazine	0.02
30. Pentachlorophenol	0.01
32. Trichlorobenzenes (1,2,4-trichlorobenzene)	0.1
33. Trifluralin	0.003

EQS: Environmental Quality Standards.

Table 3. - The procedure to assess the environmental quality standards of priority micropollutants

Micropollutant EQSs	Ecotoxicological tests (*)	Safety factors
Concentration levels with no effects on ecosystem	At least on $L(E)C_{50}$ for each trophic level (*)	1000
	One chronic NOEC (for fish, daphnia or an organism representative of salty water)	100
	Two chronic NOEC for two trophic levels (for fish, daphnia or an organism representative of salty water)	50
	Chronic NOEC for at least three species (fish, daphnia or an organism representative of salty water) belonging to three trophic levels	10
	Any other cases that allow more precise safety factors to be used	
	Case by case assessment	
Persistance or bioaccumulation	To fix EQS	
Intercalibration	EQS for public intercomparison	

(*) Three trophic levels: algae or macrophite, daphnia or organisms representative of salty water.
NOEC: No Observed Effect Concentration.
EQS: Environmental Quality Standard.

technical implications of sediment monitoring. AMPS intends to summarise the key issues and give technical expert advice to the European Commission on analysis and monitoring aspects, in order to justify the choices made in the forthcoming proposal for a daughter Directive on priority substances.

AMPS proposes the following definition for sediment: particulate material such as sand, silt, clay or organic matter that has been deposited on the bottom of a water body and is susceptible to being transported by water [8].

The purpose of analysing the levels of priority substances in sediments under the WFD are:

a) monitoring the progressive reduction in the contamination of priority substances and phasing out of priority hazardous substances; and

b) demonstrating conditions of “no deterioration” in sediment quality. This is implicit in the need to ensure adequate provision of pollution prevention and control [8].

Four types of monitoring relate to the WFD:

1) risk assessment, for instance by applying the sediment quality Triad [8] for an initial indication of the likely causes of a waterbody’s poor ecological status;

2) trend monitoring, providing an indication of increases or decreases in concentrations of contaminants over time;

3) spatial monitoring, providing an indication of the status of contamination over a given area;

4) compliance monitoring, for checking if pre-set sediment EQS are met.

Furthermore, sediments have an impact on ecological quality because of their quality or quantity, or both. Therefore, sediment monitoring programmes should also address the basic physical-chemical properties of sediments (grain size distribution, organic carbon content etc.) as well as the geomorphological processes within each river system, including those operating in floodplains, wetlands and the coastal zone. The physical-chemical quality of sediments is featured in the definition of good and moderate ecological status in rivers and lakes (Annex V 1.2). However, as this issue is not related to priority substances, it is outside the scope of the discussion document [9].

In Italy, ecotoxicology has found a place with the Legislative Decree no. 152 (May 11, 1999) [10] emanated to adopt the Directives 91/271/CEE “Urban waste-water treatment” and 91/676/CEE “Protection of waters against pollution caused by nitrates from agricultural sources”. This decree in reality goes beyond (actually, the WFD is still in progress) and charges the Regions with the duty to identify, for all water bodies, the class of quality on the basis of chemical and biological monitoring and their classification according to the environmental quality objectives.

Table 4. - EQSs of the Italian legislation for priority pollutants in sediments of salty and marine waters

	Substances	Concentration
Metals (mg/kg ss)		
	Arsenic	12
HPP	Cadmium	0.3
	Chromium (total)50	
	Cr(VI)	5
HPP	Mercury	0.3
PP	Nickel	30
PP	Lead	30
Organometals (mg/kg ss)		
HPP	Tributyltin	5
Polyaromatic hydrocarbons (PAH) (mg/kg ss)		
HPP	PAH (total)	200
HPP	Benzo(a)pyrene30	
HPP	Benzo(b)flouranthene	40
HPP	Benzo(k)fluoranthene	20
HPP	Benzo(g,k,i)fluoranthene	55
HPP	Indopyrene	70
HP	Anthracene	45
HP	Fluoranthene	110
HP	Naphthalene	35
Pesticides (mg/kg ss)		
	Aldrin	0.2
HPP	Alfa hexachlorcyclohexane	0.2
HPP	Beta hexachlorcyclohexane	0.2
HPP	Lindane	0.2
	DDT	0.5
	DDD	0.5
	DDE	0.5
	Dieldrin	0.2
HPP	Hexachlorobenzene	0.1
	Dioxin Furan (mg/kg)	
	Sum of PCDD, PCDF,	0.00015
	PCB dioxin-like (TE)	(provisional)
	PCB (mg/kg)	
	PCB (total)	4 (provisional)

EQS: Environmental Quality Standards.

In the Italian list of priority substances [11] there are six priority heavy metals. For the sake of classification of any water body according to its overall environmental quality status, the presence of micropollutants at a concentration above or below the EQS established for that substance according to the procedure of Table 3 should be assessed. In fact the environmental status is assumed as the ecological status as defined by the WFD integrated with the chemical status related to the presence of micropollutants. The detection of just one micropollutant at a concentration exceeding the EQS stands for a bad environmental status.

The EQSs officially defined are given elsewhere [11]. Their values to protect living organisms (and not only human beings) are quite low, as reported in Table 2 for the priority pollutants identified in Annex X of the WFD. Moreover, Italian legislation set a limited number of EQSs for sediments in salty and marine waters (Tab. 4).

The EU approach is taken as a reference also in countries outside the Union. As an example, the policy of the Republic of Armenia [12-14] is to include the objective of harmonizing the legislation with that of the EU.

Micropollutants and sediments in rivers

The sedimentation process causes great problems worldwide by raising the cost of operation and maintenance and complicating the design of water structures. The problems linked to sediments create difficulties in managing water systems. About 1% of the world's water storage capacity is lost every year through sediment deposition in reservoirs.

Many of the large international rivers such as, e.g., the Nile, Mississippi and Yellow Rivers carry huge amount of sediments. It is known that the Fraser River in Canada carries an average of 20 million tons of sediment each year, the Nile River carries an amount that exceeds 140 million tons annually and the Yellow River in China carries an annual amount of sediment that is several times more than that of the Nile River.

For the assessment and management of contaminated sediments in different countries chemical data have been used by state and federal regulatory agencies. For better defining the relationship between sediment chemistry and toxicity, providing regulatory agencies with additional insight into the importance of sediment chemistry data, Sediment Quality Guidelines (SQGs) [15, 16] have been developed over the last years. Increasing interest in the development of risk-based sediment assessment frameworks to guide assessments and management decisions has led to questions concerning the role of SQGs within a sediment assessment and management process that makes use of multiple Lines Of Evidence (LOE) [16] to reach management decisions based on Weight-Of-Evidence (WOE) [17]. At the moment nearly 20 sediment assessment frameworks have been proposed or used by regulatory authorities in different countries.

In Europe the Working Group AMPS has prepared a strategic paper, which in turn, was the basis for a recently prepared SedNet brochure entitled *Sediment, a valuable resource that needs Europe's attention* [18, 19].

In brief, sediments are an essential, integral and dynamic part of river basins. Sediments in rivers are an important habitat as well as a major nutrient source for

Table 5. - Descriptive statistics of annual mean concentrations of total heavy metals in European rivers (source: NERI and EEA-TF from multiple sources)

Metal	Number of river stations	Drinking water standard (μg/l)	Percentage of river stations with concentrations not exceeding a given concentration (in μg/l)			
			25%	50%	75%	90%
Cadmium	145	5(*)	0.0	0.0	0.4	1.8
Chromium	56	50(*)	1.3	4.3	11.5	17.0
Copper	192	100-3000(**)	1.6	4.8	8.0	16.0
Lead	72	50(*)	0.8	2.7	6.7	11.0
Mercury	163	1(*)	0.0	0.0	0.2	1.1
Nickel	48	50(*)	0.8	4.3	11.5	17.0
Zinc	176	100-5000(**)	5.0	10.4	36.0	91.0

(*) Maximum admissible concentration. *(**)* Guide level as specified in Council Directive (80/778/EEC).

aquatic organisms. Sediments are also used as farmland and as a source of minerals and materials. Stimulated by the WFD, the view on sediments is changing to the recognition of the key role that sediments play naturally in the river systems. Sediment management should fit into the holistic view of the role of sediments in river basin systems. This means that transboundary management is needed for river systems that cross water bodies and national borders.

Therefore, in the opinion of SedNet, the WFD represents a great opportunity and stimulus to come up with guidance for sustainable sediment management. The current scope of the WFD does not yet specifically deal with this subject. Sustainable sediment management should eventually become an integrated part of the WFD. The requirements for a river basinwide sediment concept will be even more challenging [20] that the current WFD.

General assessment of the state of heavy metal pollution of European rivers is difficult, primarily because measurement of metals is rarely included in monitoring programmes, but also because concentration levels are usually so low that problems arise with sample preparation and analytical accuracy. Until recently, metals have generally been determined either for their total concentration in water or their concentration in the suspended particulate fraction. Recent evidence, however, suggests that anthropogenic inputs generally can be better evaluated from associated particulate metals [21]. Comparison and assessment of the state of heavy metals in European rivers is thus even more difficult than for most of the other water quality parameters (see Table 5).

A general overview of the riverine transport of water, sediments and pollutants to the Mediterranean sea, as published by UNEP/MAP in 2003 (MAP Technical Reports Series no. 141) points to the fact that in Italian rivers, e.g., in the Po River, when pH = 7-8.5, most heavy metals are not dissolved: Cd, Cu, Hg, Pb, Zn are adsorbed on the surface of the suspended particles. In such cases particulate matter is normally by far the dominant transport form for heavy metals in these rivers. For example, the percentage of the load of heavy metals associated with particulate matter in the Po River is as follow [21-23]: Al, 98.4%; As, 23.0%; Cd, 41.0%; Co, 94.7%; Cr, 88.2%; Cu, 73.0%; Hg, 78.4%; Pb, 93.1%; Zn, 71.1%.

Recent investigations concerning the average dissolved trace metal concentration in Italian rivers have shown that elevated levels were as a rule found, e.g., in the Po (Cd, Cu, Ni, Zn), the Tiber (Pb, Zn) and the Arno (Cd) Rivers, although a direct comparison is not always possible because of differences in the reference periods corresponding to the values.

Table 6 summarizes the average heavy metals contents in the total suspended particulate matter for Italian rivers.

Some interesting aspects can be seen in the relative abundance of the trace metals. In the Po River, the heavy metals concentrations are elevated for most of these elements, i.e., Cd, Cr, Cu, Hg, Ni and Zn. In the Tiber River there are high concentrations of Cd, Cu and Zn, while in the Adige and Bradano Rivers Cd may raise some concern. These values also should be assessed along with the geological and lithological patterns of the river drainage basins, but this is beyond the scope of such studies.

Also trace organic compounds play a major role in river pollution. In many cases, pollution in rivers is also accompanied by organic micropollutants. Traditional monitoring for organic micropollutants in the aquatic environment has focused on organochlorine

Table 6. - Average concentration of particulate trace metals in μg/g in some Italian rivers over the period 1985-1996

River	Element							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Adige	25.3	1.2	60.7	76.6		44.6	72.7	212.0
Arno			159.0			112.0		
Bradano		2.6						
Brenta							145.0	
Po	7.0	1.7	124.0	75.0	1.54		75.0	342.0
Tiber		2.0		100.0			130.0	47.0

compounds (e.g., DDT and PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs). However, organic micropollutants have rarely been included on a large-scale basis in national monitoring programmes. Moreover, in recent years there has been a growing awareness of the problem of aquatic pollution by other dangerous compounds, such as non-organochlorine pesticides. Assessment of the environmental risk posed by pesticides must be based on a combination of studies of their impact on the aquatic biota and model calculations of potential pesticide runoff.

It is widely acknowledged that sediments play a fundamental role for the health of the aquatic ecosystems as they offer a habitat to many organisms and support to all the aquatic fauna. The sediments have been often defined as the sink of persistent substances to accumulation in this compartment. Therefore, also for sediments, a sounder approach ensues from the integration of chemical, biological and ecotoxicological data.

Sediments also represent the compartment where the vast majority of the most dangerous, persistent and accumulation-prone pollutants are deposited. They not only exert effects on the benthic organisms, but can also endanger all the aquatic life at its various levels through the food web because of their re-suspension in the water column [25]. Toxicological analyses of sediments can supply very important information about the state of health of water bodies, first of all in the case where the plain analysis conducted on the water column does not point to a significant risk.

Biological and toxicological investigations of sediments constitute a complementary approach in the appraisal of their quality with peculiar advantages and limits [26-28]. The benthic communities react to changes in the quality of water, sediments and the habitat in general. The variations in the structure of the communities supply important information directly relevant for the assessment of the contamination impact. In other words, they are important for the effects *in situ*, although they are not diagnostic for contamination or toxicity themselves. In fact, the integration of all the biotic and non-biotic factors, implicit in biological analyses, cannot distinguish among stressful factors of chemical, physical and biological type.

The integration of the biological and toxicological indexes allows the limits of these two approaches to be circumvented, thus reducing the uncertainty of the risk assessment and allowing the interventions to be planned for the attainment of objectives of ecological quality.

Among the various sediments toxicity testing phases, interstitial water plays a major role for assessing the effects *in situ* since the benthic organisms are exposed to it directly. Studies have shown that the toxic concentrations in sediments were correlated to the concentrations in interstitial water and the dissolved fraction of the pollutants is considered in many cases to be bioavailable. Tests on pelagic and benthic species exposed to several phases of sediments of various nature and contamination degree have demonstrated that interstitial water represents a suitable means to forecast global sediment toxicity [29].

River sediments are saturated with interstitial water, which favours mobilization and separation of the polluting substances. Particularly, lipophilic (or hydrophobic) substances characterized by high values of the octanol-water partition coefficient ($\log K_{ow} \geq 3$), are preferentially absorbed onto suspended material and, after sedimentation, are embodied within the sediment. Due to these characteristics, such substances tend to be significantly bioaccumulated along the trophic chain and therefore are potentially very dangerous for their ability to produce toxic effects in the biota.

River sediments represent the main sink for micropollutants in the river environment. Sediments release the micropollutants in the water environment and this process depends on the environmental conditions. Changes in the environmental conditions can lead to significant changes in the pattern of the release of micropollutants in water from sediments. Such phenomena can take place in strongly polluted areas or when environmental changes are dramatic.

As regards Italian legal provisions on water protection, the Decree DL.vo. 152/99, in Paragraph 3.2.1.3, Annex 1, prescribes that the analysis of river sediments should be considered as additional and optional, as it is useful to elucidate chemical parameters and ecological descriptors.

Pesticides have become an important part of modern agriculture and their use has been growing exponentially every year after the Second World War because of the increasing food demand. In spite of the undeniable advantages that pesticides have brought to modern economy, the phytosanitary products can generate a series of problems for untargeted animal species as well as for human health. Many pesticides and also some of their products of degradation can be found today in surface as well as in groundwaters. Some compounds, through the processes of erosion and streaming or drifting, can come in contact with surface water bodies and contaminate the sediments. The linkage of pesticides to sediment particles delays their migration and increases their persistence with potential risks to ecosystems [30]. Natural or xenobiotic substances released into the environment follows a specific biochemical cycle that determines their transport and distribution, which in their turn depend on the partition processes. Obviously the biogeochemical cycle of a substance and its environmental fate depend on the characteristics of the various compartments as well as from environmental parameters.

On the other hand, when environmental conditions are stable, the partition and the fate of an ionisable substance depend on its inherent properties, such as solubility, KH, K_{ow}, K_{oc}, DT_{50} and pH [31]. As already said, the sediments of an aquatic environment are saturated with interstitial water, which favours the transport and partition of pesticides. Moreover, this kind of water contains Dangerous Organic Materials (DOMs), i.e., colloids and other macromolecules that can bind these substances, thus facilitating their transport and bioavailability. It has been demonstrated that pesticide particles of small dimensions are distributed at greater concentrations in the sediment fractions containing small particles (<6.3 µm) or large particles (63-200 µm), probably because these fractions contain more organic material [30].

For the time being, a relation has been found between the contents of organic material of sediments and their adsorption ability for chemical substances, in particular for non-ionic organic compounds. Another parameter that influences the adsorption ability is pH, this being particularly obvious in the case of s-triazine-type herbicides. The maximum adsorption takes place when pH is close to the values of pKa (1.7-2.6). At this pH half of the s-triazine compounds is in the cationic form and the other half is in the not-ionic state. The increase in pH results in a decrease of the cationic fraction in the solution and, therefore, in lesser adsorption.

Other pesticides can be adsorbed as a consequence of weak bonds like the hydrogen bonds and the Van der Waals' forces. Non-ionic compounds probably interact with sediments through hydrophobic connections little affected by pH.

Conclusions

The use of potentially toxic substances (e.g., DDT, PCBs) has been either restricted or banned in several European countries during the last 30 years. As a result, there has been a marked reduction in their levels in rivers. However, other organic micropollutants suspected of having detrimental environmental effects, as well as many with so far unknown effects, are still being discharged into freshwater bodies.

Sediments are an essential, integral and dynamic part of European river basins. It is an important habitat as well as a major nutrient source for aquatic organisms. Sediments are also used for farmlanding and as a source of minerals and materials. Prompted by the WFD, views on sediments are changing and now recognize the key role they play in the preservation of river systems. Sediment management should fit into the holistic view of the role of sediments in river basin systems. This means that transboundary management is needed for river systems that cross national borders.

Sediments have an impact on ecological quality because of their inherent characteristics. Therefore, sediment monitoring programmes should be set up and address also their basic physical-chemical properties as well as the geomorphological processes within each river system, including those operating in floodplains, wetlands and coastal zones.

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REFERENCES

1. GEO: Global Environment Outlook Year Book 3, 2003, http: //www.unep.org.

2. European Parliament and the Council. Official Journal of the European Communities, Directive 2000/60/EC of the 23 October 2000 establishing a framework for Community action in the field of water policy L 327, p. 1 ff.

3. Official Journal of the European Communities, Council Directive 96/82/EEC, L10, p.13 ff.

4. Official Journal of the European Communities, Council Directive 22 December.1988 on the approximation of laws, regulations and administrative provisions of the Member States relating to construction products, 1988, L 40, p. 12 ff.

5. Official Journal of the European Communities 18 May 1976 L 129,0023-0029.

6. Official Journal of the European Communities 15 December 2001, L331.

7. EU Directive 20 July 1993 n° 67 laying down the principles for the assessment of risks to man and the environment of substances notified in accordance with Council Directive 67/548/EEC. Official Journal of the European Communities, L227.

8. Chapman PM. Presentation and interpretation of sediment quality triad data. *Ecotoxicology* 1996;5:327-39.

9. Stronkhorst J, Brils J, Batty J, Coquery M, Gardner M, Mannio J, O'Donnell C, Steenwijk J, Frintrop P. *Sediment monitoring guidance for the EU water framework directive. W.G, on analysis and monitoring of priority substances*. (Discussion Document, May 25th, 2004).

10. Italia. Decreto Legislativo 11 maggio 1999, n.152. Disposizioni sulla tutela delle acque dall'inquinamento e recepimento della direttiva 91/271/CEE concernente il trattamento delle acque urbane e della direttiva 91/676/CEE relativa alla protezione delle acque dall'inquinamento provocato dai nitrati provenienti da fonti agricole a seguito delle disposizioni correttive ed integrative di cui al decreto legislativo 18 agosto 2000, n. 258. Supplemento Ordinario n.172 *Gazzetta Ufficiale* 246, 20 ottobre 2000.

11. Italia. Decreto Ministeriale 6 novembre 2003, n. 367. Regolamento concernente la fissazione di standard di qualità nell'ambiente acquatico per le sostanze pericolose, ai sensi dell'articolo 3, comma 4, del DL.vo 11 maggio 1999, n. 152. *Gazzetta Ufficiale* n. 5, 8 gennaio 2004.

12. Association for Sustainable Development (UNEP National Committee). *The concept of sustainable development of the Republic of Armenia*. Yerevan, 2002.

13. Ministry of Nature Protection of the Republic of Armenia. *National programme to combat desertification in Armenia*. Yerevan, 2003.

14. National Statistical Service of the Republic of Armenia. *Environment and natural resources of the Republic of Armenia*. Statistical Collection, Yerevan, 2003.

15. MacDonald DD, Ingersoll CG, Berger TA. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 2000;39: 20-31.

16. MacDonald DD, Ingersoll CG. Guidance manual to support the assessment of contaminated sediments in freshwater ecosystems. Washington: USEPA; 2002. (905-B02-001-A).

17. Burton GA, Batley GE, Chapman PM, Forbes VE, Schlekat CE, Smith PE, den Besten PJ, Barker J, Reynoldson T, Green AS, Dwyer RL, Berti WR. A weight-of-evidence framework for assessing sediment (or other) contamination: Improving certainty in the decision-making process. *Human Ecol Risk Assessment* 2002;8(7):1675-96.

18. European Sediment Research Network SedNet. The SedNet Strategy Paper: Abatement of water pollution from contaminated land, landfills and sediments. 2003 June. Downloaded from www.SedNet.org.

19. European Sediment Research Network SedNet Sediment, a valuable resource that needs Europe's attention. 2004 downloadable through: http://www.sednet.org/newsitem.asp?ni=106

20. Förstner U. Sediments and the European Water Framework Directive. *J Soils Sediments* 2002;2(2):5.

21. Meybeck M, Chapman D V, Helmer R. Global freshwater quality: a first assessment GEMS: Global Environmental Monitoring System. WHO/UNEP 1989, Blackwell, Cambridge Eds.

22. Pettine M, Camusso M, Cogliati N, Ferrara R, Martinotti W. Fattori di variazione della concentrazione dei metalli. CNR, Quaderno IRSA 1991;92: p. 3.1- 3.5

23. Pettine M, Mastroianni D, Camusso M, Guzzi L, Martinotti W. Distribution of As, Cr and V species in the Po-Adriatic mixing area. *Mar Chem* 1997;58: 335-349.

24. Galassi S, Guzzella L, Mingazzini M, Vigano L, Capri S, Sora S. Toxicological and chemical characterization of organic micropollutants in river Po waters. *Water Res* 1992;26:19-27.

25. Power, EA, Chapman, PM. Assessing sediment quality. In:. Burton, GA (Ed). Contaminated sediment toxicity assessment, CRC Press, Inc., Florida, 1992.

26. Tonkes M, Van Der Guchte C, Botterweg J, De Zwart D, Hof M. Monitoring water quality in the future. Volume 4, RIZA, Lelystad, Neederlands. 1995.

27. ASTM Standard guide for collection, storage, characterization, and manipulation of sediments for toxicological testing. Annual Book of ASTM Standards 2003.

28. USEPA. A guidance manual to support the assessment of contaminated sediments in freshwater ecosystems. 2002, Vol III. (EPA-905-B02-C).

29. Ankley GT, Scubauer-Berigan MK, Dierkes LR, and Lukasewycz MT. National Effluent Toxicity Assessment Center, 1992. (EPA 600/6-91/007).

30. Gao JP, Maguhn J, Spitzauer P, Kettrup A. Distribution of pesticides in sediment of the small Teufelsweiher pond. *Water Res* 1997;31(11):2811-9.

31. Vighi M and Di Guardo A. Predictive approaches for the evaluation of pesticide exposure. In: Vighi M and Funari E. (Eds.) *Pesticide Risk in Groundwater*. Boca Raton FL, USA.: Lewis Publishers; 1995.