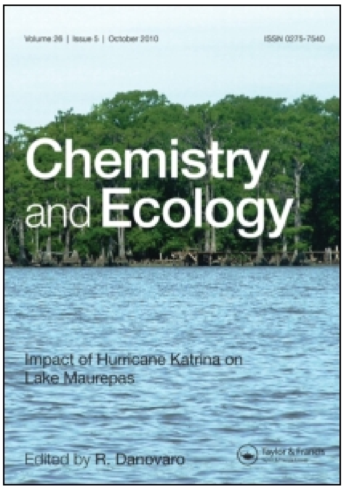

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Implementation of Directive 2000/60/EC: risk-based monitoring for the control of dangerous and priority substances

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The 2000/60/EC *Water Framework Directive* sets out a new approach for the assessment and management of chemical pollutants (i.e. formerly dangerous substances) in water bodies. The list of main classes of pollutants was revised and a detailed list of priority substances, including priority hazardous substances, has been provided. Moreover, the Directive asks for additional priority substances to be identified at national and river catchment level. The implementation of the Directive requires the monitoring of the main pollutants after the identification of the priority and dangerous substances potentially discharged into each river catchment area, together with the definition of the *Environmental Quality Standards*. In this paper, an approach based on the integration of the *Driving force-Pressure-State-Impact-Response* model with the *Environmental Risk Assessment* as a support methodology for the monitoring management (i.e. choice of priority substances, quantification of *Environmental Quality Standards*, identification of interventions) is presented. In addition, a case study on the assessment of monitoring data concerning industrial and municipal discharges, and the surface waters of the Venice lagoon catchment area is discussed. Since 1998, very strict environmental quality standards and discharge limits have been enforced in the lagoon of Venice and its catchment area. The experience gained from this monitoring is used to highlight the implementation issues concerning the *Water Framework Directive* and to identify the priority substances which can pose a significant risk for freshwater ecosystems.

Keywords: dangerous substances; priority substances; priority hazardous substances; environmental quality standards; DPSIR model; environmental risk assessment; limit of detection; limit of quantification

1. Introduction

Natural waters, which are essential for the maintenance of the environment and the protection of human health, are threatened by several factors, including dangerous substances, also called pollutants. The first European regulatory approach to pollutants dates back to the 1970s with the 76/464/EEC directive [1], which established the criteria of hazard classification (i.e. persistence, toxicity, bioaccumulation) and identified the classes of major pollutants. The recent *Water Framework Directive* (WFD) 2000/60/EC [2] included issues concerning dangerous, priority and

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priority hazardous substances, together with those of a more general nature, for the assessment and management of the environmental quality of water bodies.

Accordingly, the major objectives of this work are twofold: (i) to highlight the new measures introduced by the WFD concerning the main pollutants, such as the need for the Member States to formulate and enforce *Environmental Quality Standards* (EQSs); and (ii) to demonstrate the benefits resulting from the integration of the *Driving force-Pressure-State-Impact-Response* (DPSIR) model with the *Environmental Risk Assessment* (ERA). The latter appears to be essential regarding the design of monitoring activities to support the WFD implementation.

As a case study, we are to present a screening application of the DPSIR-ERA approach to the catchment basin of the Venice lagoon. The results of the monitoring of some of the main pollutants in surface waters and the effluents from industrial and mixed (industrial and municipal) wastewater treatment plants (WWTPs) located in the Venice lagoon catchment area are illustrated in this paper. The ERA screening system was used for the preliminary identification of the substances to be monitored and controlled, and consequently for the management of the residual risk.

The monitoring of the new priority and priority hazardous substances requires a great deal of analytical input, in order to comply with the detection/quantification limits (LOD/LOQ) established by the new EQSs. The development of more adequate analytical methods, which are still not available today and are not completely reliable, and the optimisation of the existing analytical techniques are essential requirements for the proper implementation of these studies. Therefore the questions we deal with in this paper are: 'What substances should be controlled?' and 'How can we control them?'

1.1. *An outline of the former and present approaches to the regulation of dangerous and priority substances*

A description of the shift from the former to actual approach to the regulation is presented in Figure 1, which gives a schematic classification of dangerous substances and outlines the formulation of the EQSs regarding the protection of human health and natural ecosystems at European, national and local (i.e. river basin) scale. The old approach was based on lists I and II of the dangerous substances contained in the 76/464/EEC directive, which was aimed at eliminating the emission of substances in list I and a reduction in the emission of the substances in list II. The WFD replaced the former lists I and II with a new generic list of substances and classes of substances, i.e. '*the indicative list of main pollutants*' which is given in Annex VIII of this directive. In Table 1, the combining of lists I and II with the new *indicative list of main pollutants* is reported. Noticeably, the new list of main pollutants extended the former list I to include substances 'which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment'.

In addition to the generic list of main pollutants, the WFD provided a list of priority pollutants, identifying two categories of substances for which specific measures (i.e. interventions) should be taken: *Priority Substances* (PS) (substances listed in Annex X of the WFD (modified following decision 2455/2001/EC [3])) and *Priority Hazardous Substances* (PHS). The PSs are those substances which pose a significant risk both to or via the aquatic environment, including the risks associated with the use of surface waters in drinking water production. The PHSs are the PSs which are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern.

As far as chemical substances are concerned, the WFD demands the achievement of a '*good chemical status*' regarding surface waters and ground-waters within 15 years from its enforcement (i.e. by the year 2015). The above refers to the status to be reached in a water body, which should indicate concentrations of chemical pollutants not exceeding the EQSs as defined in the same

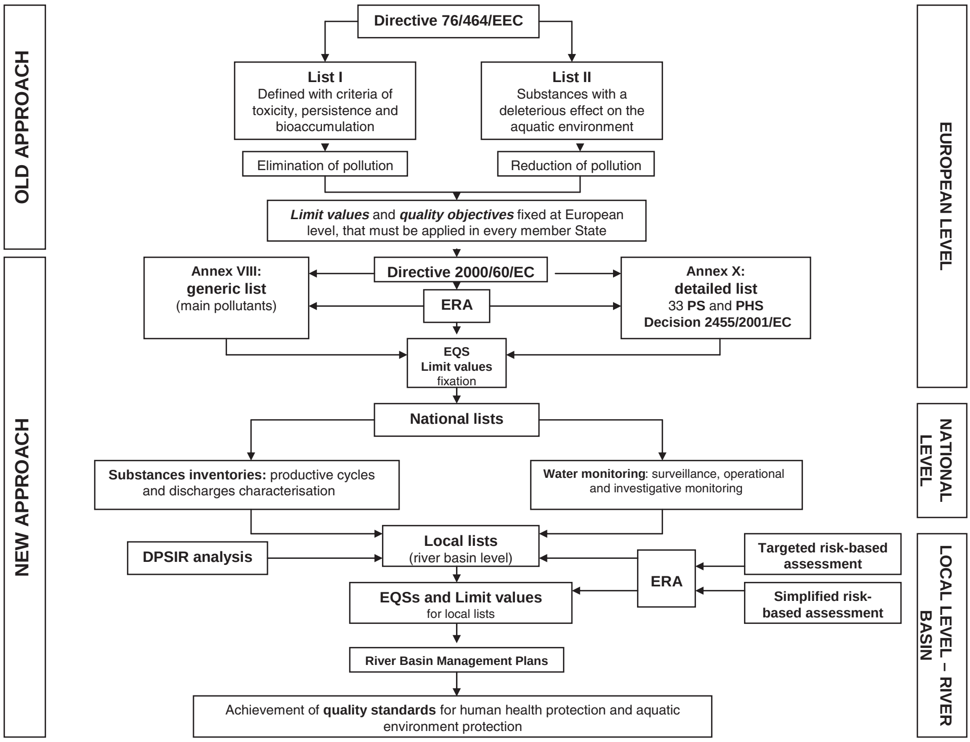

Figure 1. Flow chart describing the main features of directives 76/464/EEC and 2000/60/EC (WFD), respectively, with reference to dangerous/priority substances. Abbreviations: DPSIR: Driving force-Pressure-State-Impact-Response; ERA: Environmental Risk Assessment; PSs: priority substances; PHSs: priority hazardous substances.

Table 1. List of main classes of pollutants in accordance to the WFD (Annex VIII) together with the indication of the corresponding classes in Lists I and II of Directive 76/464/EEC.

List of main pollutants (Directive 2000/60/EC)	Correspondence with list in Directive 76/464/EEC
1. Organohalogen compounds and substances which may form such compounds in the aquatic environment.	List I point 1
2. Organophosphorous compounds.	List I point 2
3. Organotin compounds.	List I point 3
4. Substances and preparations, or the breakdown products of such, which have been found to possess carcinogenic or mutagenic properties, or properties which may affect steroidogenic, thyroid, reproductive or other endocrine-related functions, in or via the aquatic environment.	List I point 4 (enlarged)
5. Persistent hydrocarbons and persistent and bioaccumulable organic toxic substances.	List I points 7 and 8 (enlarged)
6. Cyanides.	List II point 7
7. Metals and their compounds.	List I points 5, 6 and List II point 1
8. Arsenic and its compounds.	List II point 1
9. Biocides and plant protection products.	List I point 8, List II point 2
10. Materials in suspension.	List II point 8
11. Substances which contribute to eutrophication (in particular, nitrates and phosphates).	List II points 5 and 8
12. Substances which have an unfavourable influence on the oxygen balance (and can be measured using parameters such as BOD, COD, etc.).	List II point 8

directive. In regards to chemical pollutants, the substances mentioned in Annex VIII of the WFD, together with the PSs and PHSs, must be considered.

The ultimate goal of the WFD is to ensure the attainment of a *High ecological status* by means of a short to mid-term (2008–2015) achievement of a *Good ecological status*. Biological, hydromorphological and physico-chemical quality elements all contribute to the ecological status of a water body. The PSs, PHSs and other dangerous substances must show concentrations below those stipulated by the EQSs, which is the indicator of a good chemical status. The procedure regarding the definition of the EQS is outlined in Annex V of the WFD. Tests for both acute and chronic toxicity, plus the use of specific *safety factors* for the determination of the final standards, are required in this case.

According to the new European policy on priority substances (the '*new approach*' in Figure 1), the number of substances to be controlled has increased considerably, due to the integration of the criteria regarding *toxicity*, *persistence* and *bioaccumulation* with those concerning the *risk for the aquatic environment*. The setting of the PSs, PHSs and EQSs should be based on the risk assessment, as indicated in art. 16 of the WFD, in accordance with the reference procedures (regulation n. 793/1993, directive 91/414/EEC, directive 98/08/EC). Furthermore, the need to prioritise interventions concerning the risk to, or via, the aquatic environment, triggers of a *simplified risk-based assessment procedure*, 'based on scientific principles'. However, in regards to the implementation of this simplified procedure, the following guidelines must be taken into account:

- evidence regarding the intrinsic hazard within each substance of concern and, in particular, of its aquatic eco-toxicity and toxicity to humans via aquatic exposure routes;
- evidence of widespread environmental contamination, received from monitoring procedures;
- other proven factors which may indicate the possibility of widespread environmental contamination, such as the production of, or use in volume, of the substance of concern, combined with the patterns of use of the same substance.

The list of PSs (WFD Annex X – '*Priority substances*'), established by the European Council Amendment n. 2455/2001/EC [3], contains 33 substances, or classes of substances, which were selected using a procedure based on the principles of monitoring and modeling: COMMPS (the combined monitoring-based and modeling-based priority setting procedure) [4]. It should be noted that a further period of testing of some PSs is required before they can definitively be listed as priority substances.

In addition to the list of 33 priority substances already identified by the WFD, it is to be expected that a further list of PSs will be provided by each Member State on a national scale, and another list should be drawn up on a river basin scale. In Italy, the identification of these substances should be made by the local authorities (regions) which must propose the local list to the National Authority (State, Ministry of the Environment) responsible, by law, for the setting of the water EQSs.

1.2. *The control and management of dangerous and priority substances through the setting of environmental quality standards and limit values*

The control and management of dangerous and priority substances needs the implementation of an environmental management model with a sound knowledge of environmental concentrations and pressure sources. Article 10 of the WFD establishes that all point and non-point (i.e. diffuse) emission sources into surface waters must be controlled using a *combined approach*: i.e. the control of the emissions based on the use of the Best Available Technologies (BAT); the control of the emission limit values; the application of the best environmental practices concerning diffuse sources. With regards to the characterisation of the pollution from the anthropogenic point and the diffuse pressure sources, the information concerning pollution caused by substances contained in Annex VIII of the WFD (list of main pollutants) must be consulted. An inventory analysis of industrial cycles and diffuse pollution sources is of utmost importance.

The WFD has established a methodological approach regarding both environmental quality assessment and management, in accordance with Arts. 5, 8, 10 and 13, which are in practice based on the DPSIR (*Driving force-Pressure-State-Impact-Response*) conceptual model. The DPSIR model is a decisional framework for environmental management. It had previously been proposed by the OECD and was subsequently modified by the European Environmental Agency [5].

Moreover, it is anticipated that the *Environmental Risk Assessment* (ERA) approach, which uses water quality monitoring and characterisation of the pressure sources, will be employed for the identification of the priority pollutants, the definition of the emission limits regarding discharges and in regards to the identification of the EQSs for the receiving water bodies. The objective to be considered here is to establish of a support mechanism concerning the DPSIR framework, with the aim of defining the specific measures needed to reach the fixed quality objectives. The DPSIR model had already been used at river basin level and is widely recognised as an effective assessment and intervention method; this model appears to be particularly suitable for the integration of the monitoring and management of dangerous and priority chemical substances within the *River Basin Management Plans* (RBMPs) as indicated in the WFD Directive [6,7].

Most priority substances have, in practice, already been regulated by means of national EQSs, which vary considerably from State to State. The EQSs for priority substances should be established on a European scale, in order to ensure the maintenance of similar levels of environmental protection. This criterion must be reached, in order to meet the specific demands of the WFD, achieving harmonisation and consistency among the Member States concerning Community legislation, while leaving each Member State free to fix their EQSs for other main pollutants. In regards to the eight dangerous substances (DDT, Aldrin, Dieldrin, Endrin, Isodrin, Carbontetrachloride, Tetrachloroethylene, Trichloroethylene) which have not been considered as PSs but are included in list I of Directive 76/464/EEC, it was decided to fix their EQSs at a Community level too.

In accordance with Article 16, paragraph 7 of the WFD, the EC Commission presented a proposal regarding the establishment of quality standards concerning the 33 priority PSs contained in Decision n. 2455/2001. At a European level, the setting of the EQSs for the PSs and PHSs of the substances on the ‘European list’ was proposed by EC COM(2006)397 [8]. By means of this proposal, which was confirmed by the adoption of a common position on the 20/12/2007 (ENV 378 CEDEC 757) and then approved with Directive 2008/105/EC [9] on environmental quality standards for waters, the EQSs concerning the 33 priority and priority hazardous substances (reported in Table 3), plus the additional eight dangerous substances, were set in such a way as to ensure a high level of protection against risks to, or via, the aquatic environment. The common position fixes two values for each substance: (i) a *maximum allowable concentration*, as a means for avoiding serious, irreversible consequences for ecosystems exposed to acute contact in the short term; and (ii) the *annual average EQS*, used to prevent irreversible consequences in the long term. As far as metals are concerned, the Member States are allowed to adapt the compliance regime to their own needs, as background levels and bioavailability have to be taken into account in each case. The necessity to identify a transitional area concerning limit values in the vicinity of the point source discharges was decided upon for those areas of water bodies where EQSs cannot be met, due to the elevated levels of pollutants in the effluents.

With regards to the question of pollution control measures, the common position leaves the decisions concerning additional specific measures up to the Member States, who have to draw up an inventory of the emissions, discharges and losses from their river basins. Consequently, the national list should contain the PSs and PHSs fixed by the European Commission, those fixed by each Member State, plus the other dangerous substances, as a means of ensuring a complete analysis of the list of main pollutants in accordance with the actual existing pressure sources, in order to guarantee the achievement of the WFD's objectives.

Before the introduction of the COM 398 proposal (2006), each Member State had to define the EQSs for the PSs established by the Commission in 2006 in accordance with Article 16 of the WFD. In Italy, the EQSs at both national and local (river basin) level were fixed by using existing European references, whenever possible, or by introducing new EQSs. The emission values and EQSs for 18 specific pollutants were established using the 'daughter directives' of the Directive 76/464/EEC, and were also added to the Italian national list of dangerous and priority substances.

The introduction of the Italian regulation (Decree n. 367 of 6/11/2003 [10]) amended by Decree n. 152/2006 [11] finally completed the section of Directive 76/464/EEC ('the old approach') not transposed up to then into the Italian legal framework concerning the definition of the EQSs for surface fresh waters, marine-coastal waters and lagoons, combined with the definition of programmes to reduce and eliminate the pollution caused by dangerous substances. This Italian regulation identified the PSs and PHSs (according to the WFD list) and fixed the EQSs for 160 substances, distributed over a range of 10 classes of substances or categories. These are given in Table 2, together with the indication of the number of priority substances per class or category.

The Italian national list fixed two EQSs for each substance in surface waters: one to be achieved in the short term (within the year 2008) and another, more restrictive one, to be achieved in the medium-long term (within the year 2015) according to the time frame of the WFD. As for the substances not included in the national list (e.g. new synthetic substances), the ERA was identified as the methodology for fixing the EQSs for these substances. The possible application of restrictions to the water body could be introduced, based on the results of the risk assessments.

The finding that some EQSs could not be achieved using even the most advanced analytical techniques (fixed by decree n. 367/2003 for the year 2008) prompted the enforcement of a new decree (decree 3/04/2006 n. 152), as stated before, which fixed higher EQSs for selected substances on a temporary basis (Table 3), while maintaining the same EQSs up to the year 2015. The Italian national list contains the PSs, PHSs and dangerous substances, but the EQSs of COM 398 (2006), now Directive 2008/105/EC, are not included. This list is now under review, so that the implementation of the proposed European standards concerning the PSs and PHSs and the parameters indicated in the 'daughter directives' can be integrated.

The main challenge that the Regional Environmental Agencies in Italy and Europe are facing, concerning the implementation of the WFD, is the newly required monitoring system project: new parameters have to be monitored, inventories of emission sources have to be drawn up, effective measures of intervention have to be identified and new analytical methods have to be set up.

Table 2. Classes and number of priority substances included in the Italian national list and substances monitored by the ARPAV-Venice Laboratory Service in the surface waters of the Venice lagoon catchment area.

Class of substances or categories	Total number of substances per class/category	Priority substances per class/category	No. of analysed substances
Metals	6	4	6
Organometals	6	2	3
Policyclic Aromatic Hydrocarbons	9	9	6
Volatile Organic Compounds (VOCs)	37	5	14
Nitroaromatics	7	–	0
Alophenols	9	1	2
Anilines and derivatives	5	–	0
Pesticides	54	14	29
Semivolatile Organic Compounds	8	1	1
Other compounds	19	8	2
Total	160	44	63

Table 3. Environmental Quality Standards (EQSs) in the Italian (decrees n. 367/2003, n. 152/2006) and Venice lagoon (decree dated 23 April 1998) regulations for European P and PH pollutants in surface waters; limit of detection (LOD) for industrial discharges and surface waters and the analytical techniques used in achieving the LODs.

Pollutant	2008 EQS Italian Regulations (µg/l)	2015 EQS Italian Regulations (µg/l)	EQS for the Venice lagoon and its catchment area (µg/l)	EQS Directive 2008/105/EC Inland surface waters – Average annual value (µg/l)	Limit values for discharges in the catchment area of the Venice lagoon (µg/l)	LOD obtained by the Venice ARPAV for *Discharges* (µg/l)	LOD obtained by the Venice ARPAV for *Surface waters* (µg/l)	Analytical technique used to achieve the reported LOD
Cadmium PH	1ˆ	0.1 D 0.03 M-L	0.01	0.08	5§ (1§§)	0.5	0.2	ICP-MS
Mercury PH	1ˆ	0.02 D 0.003 M-L	0.005	0.01	3§ (0,5§§)	1	0.2	ICP-MS/CVAAS
Nickel P	20ˆ	1.3 D 0.6 M-L	0.5	20	100°	5	1	ICP-MS/GFAAS
Lead P	10ˆ	0.4 D 0.06 M-L	0.03	7.2	50§ (10§§)	0.5	0.5	ICP-MS
Tributyltin (compounds) PH	0.001*	0.0001	0.01	0.0002		0.03	0.03	GC/MS
Tributyltin cation PH	0.001*							
Total Policyclic Aromatic Hydrocarbons PH	0.2ˆ	0.005	0.06 (Lagoon)			0.01	0.01	HPLC/FL
Benzo(a)pirene PH	0.004 D* 0.003 M-L	0.001	0.003 (Lagoon)	0.05		0.01	0.01	HPLC/FL
Benzo(b)fluoranthene PH	0.004 D* 0.003 M-L	0.001	0.003 (Lagoon)	Σ0.03		0.01	0.01	HPLC/FL
Benzo(k)fluoranthene PH	0.004 D* 0.003 M-L	0.001	0.003 (Lagoon)			0.01	0.01	HPLC/FL
Benzo(g,h,i)perylene PH	0.004 D* 0.003 M-L	0.001	0.003 (Lagoon)	Σ0.002		0.01	0.01	HPLC/FL
Indeno(1,2,3-cd)pyrene	0.004 D* 0.003 M-L	0.001						HPLC/FL
Anthracene P	0.1 D* 0.01 M-L	0.01 D 0.006 M-L		0.1				
Fluoranthene P	0.1*	0.01		0.1				
Naphtalene P	0.1*	0.01		2.4				
Benzene P	1ˆ	0.2 D 0.1 M-L	0.1	10		1	1	GC/MS P&T
1,2,4 Trichlorobenzene P	0.4ˆ	0.01 D 0.005 M-L				0.1	0.1	GC/ECD
1,2 Dichloroethane P	10ˆ	0.3 D 0.1 M-L	0.4	10		1	1.0	GC/MS P&T
Hexachlorbutadiene PH	0.1ˆ	0.001	0.1 (Lagoon)	0.1		0.1	0.1	GC/ECD
Trichloromethane (Chloroform) P	12ˆ	1 D 0.01 M-L	5.7 (Lagoon)	2.5	400°ˆˆ	1 (0,1)	0.4	GC/ECD/HS
Di(2-ethylhexyl)phtalate P	1 D* 0.1 M-L	0.3D 0.03 M-L		1.3				

(*Continued*)

Table 3. Continued.

Pollutant	2008 EQS Italian Regulations (µg/l)	2015 EQS Italian Regulations (µg/l)	EQS for the Venice lagoon and its catchment area (µg/l)	EQS Directive 2008/105/EC Inland surface waters – Average annual value (µg/l)	Limit values for discharges in the catchment area of the Venice lagoon (µg/l)	LOD obtained by the Venice ARPAV for *Discharges* (µg/l)	LOD obtained by the Venice ARPAV for *Surface waters* (µg/l)	Analytical technique used to achieve the reported LOD
Pentachlorophenol P	0.4ˆ	0.01	0.03	0.4				
Endosulfan P	0.1ˆ	0.00001	0.009 (Lagoon)	0.005		0.01	0.01	GC/ECD
Alpha endosulfan P	0.1ˆ	0.00001						
Lindan (γ isomer of hexachlorcyclohexane) PH	0.1ˆ	0.001 D 0.0005 M-L				0.01	0.01	GC/ECD
$\alpha-$hexachlorocyclohexane PH	0.1ˆ	0.0002				0.01	0.01	GC/ECD
$\beta-$hexachlorocyclohexane PH	0.1ˆ	0.0002		0.02		0.01	0.01	GC/ECD
Hexachlorobenzene PH	0.1ˆ		0.0008 (Lagoon)	0.01		0.01	0.01	GC/ECD
Diuron P	0.1ˆ	0.02 D 0.01 M-L		0.2				
Isoproturon P	0.1ˆ	0.02 D 0.01 M-L		0.3				
Atrazine P	0.1ˆ	0.01	0.01 (Lagoon)	0.6		0.01	0.01	GC/MS
Simazine P	0.1ˆ	0.02 D 0.01 M-L	0.01 (Lagoon)	1				
Clorfenvinphos P	0.1ˆ	0.0002		0.1				
Clorphyrifos P	0.1ˆ	0.0001	0.006 (Lagoon)	0.03		0.01	0.01	G./ECD
Alachlor P	0.1ˆ	0.03 D 0.01 M-L		0.3		0.01	0.01	GC/MS
Trifluralin P	0.1ˆ	0.003 D 0.0006 M-L		0.03				
Pentachlorobenzene PH	0.03*	0.003	0.03 (Lagoon)	0.007		0.1	0.1	GC/ECD
C_{10}-C_{13}-Chloroalkanes PH	0.5 D* 0.1 M-L Temporary			0.4				
Total brominated diphenylethers PH	0.001*	0.0005		0.0005				
Nonylphenols PH	0.3 D* 0.03 M	0.03 D 0.003 M		0.3				
4(para)-nonylphenol PH	0.01 D* 0.006 M-L	0.001 D 0.0006 M-L						
Octylphenols P	0.1 D* 0.005 M-L	0.01 D 0.001 M-L		0.1				
Para-terz-octylphenol P	0.1 D* 0.005 M-L	0.01 D 0.001 M-L						

Notes: D: surface waters; L: lagoons; M: marine waters; LOD: limit of detection; ICP/MS: inductively coupled plasma mass spectrometry; HPLC: high pressure liquid chromatography; GC: gas chromatography; ECD: electron capture detector; GC/ECD: gas chromatography with ECD detector; GC/NPD: gas chromatography with NPD detector; AAS: atomic absorption spectroscopy; GC/MS: gascromatography/mass spectrometry; GC/MS P&T: gascromatography/mass spectrometry purge & trap; HPLC/FL: high pressure liquid cromatography/fluorescence detection; P: priority substances according to Decision n. 2455/2001/EC; PH: priority hazardous substances according to Decision n. 2455/2001/EC. *Decree n. 367/2003. ˆDecree n. 152/2006. ˆˆAs the sum of tetrachlorometane, chloroform, 1,2-dichloroethane, trichloroethilene, tetrachloroethilene, trichlorobenzene, easchlorobutadiene, tetrachlorobenzene. °Section 1 Tab. A Decree 30/07/1999. §Section 3 Tab. A Decree 30/07/1999 if the final wastewaters flow into a treatment plant. §§Section 4 Tab. A Decree 30/07/1999 if the final wastewaters flow directly into water bodies (more restricted table). Grey shading indicates the lowest EQSs between national lists and local lists (Venice lagoon catchment basin).

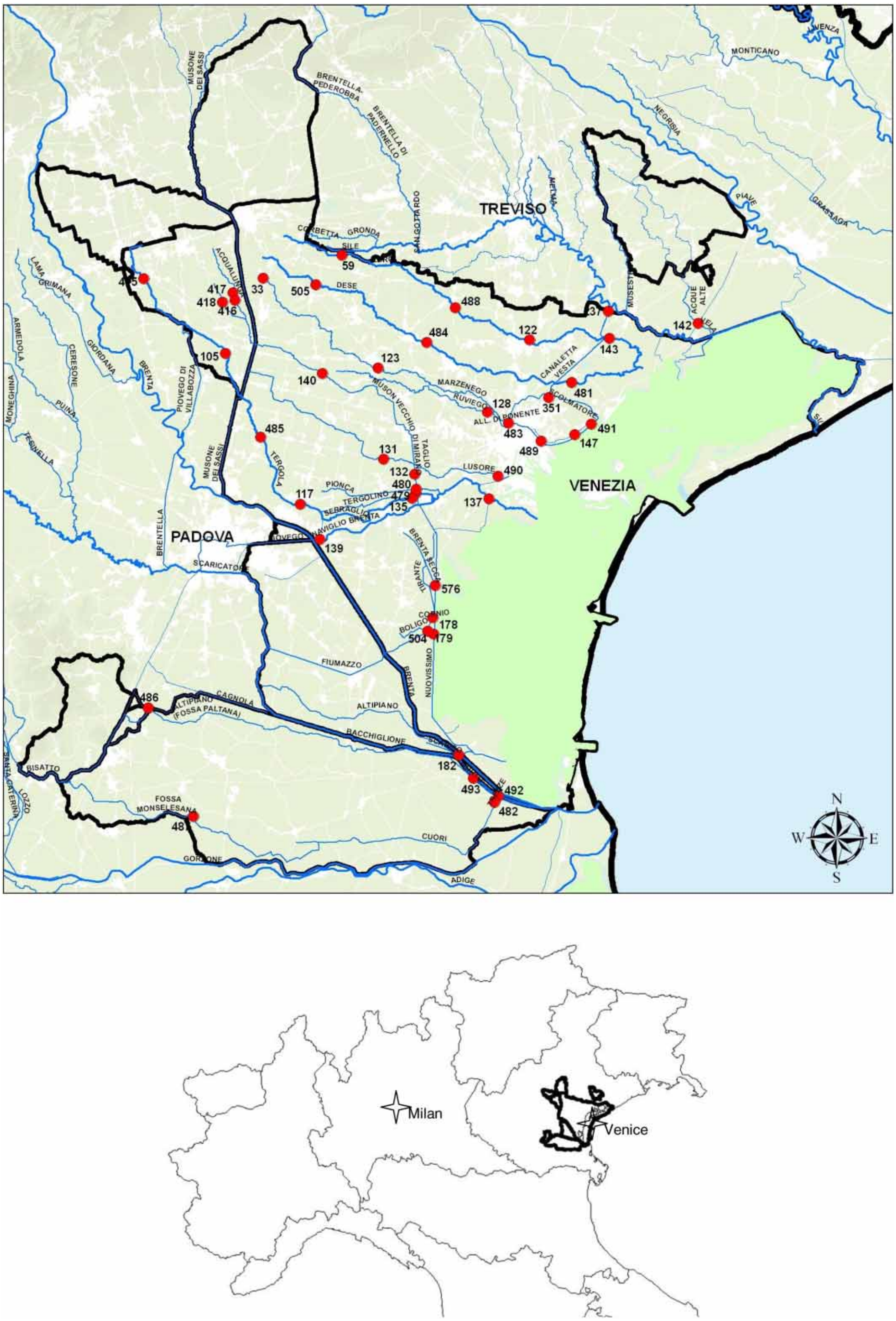

Figure 2. Map of water monitoring stations in the Venice lagoon catchment area and its location in Northern Italy (Source: Veneto Region-ARPAV, Internal Water Service 2008, itanduo@arpa.veneto.it).

1.3. *A case study: the catchment basin of the Venice lagoon*

The Venice lagoon catchment basin has a total surface area of about 1,850 km^2 and includes the Gorzone channel, which follows the Adige river in the southern part, the Euganean Hills, the

River Brenta and the River Sile (Figure 2). The land use includes: agriculture (85.9%); urban areas (9.2%); industrial areas (2.4%); green areas (1.9%) and other areas (0.6%) [12]. Freshwater enters the Venice lagoon through 24 outfalls. Of these, 11 tributaries are responsible for 97% of the total discharge: the Silone Canal, the River Dese, the Scolmatore, Osellino and Lusore Canals, and the Naviglio Brenta, Taglio Nuovissimo, Lova, Montalbano, Morto and Cuori Canals. A monitoring network is already in operation concerning the river flow measurement: a typical total annual mean flow is approx. $22\,m^3/s$ [13].

The main primary contaminant sources in the Venice lagoon and its catchment area were treated and untreated industrial and municipal effluents, the freshwater conveyed into the lagoon by rivers which contain industrial and municipal sewage, and the agricultural runoff from the drainage area [14]. Based on the assessment of the mean discharge flow, obtained by means of permits (there were 238 authorisations of industrial discharges into surface waters in the year 2003), the total annual flow of industrial discharges into the Venice lagoon catchment area was estimated in $0.76\ m^3/s$ (ca. 3.4% of the total freshwater river flow of the catchment basin).

The Venice lagoon and its catchment area are the most significant case study in Italy for the monitoring of dangerous and priority substances in surface waters and wastewater effluents, because of the special regulations which have been in force since 1998 (concerning water quality standards [15], the prohibition of discharges of specific substances [16], the establishment of the maximum admissible pollution loads [17], the application of the best available technologies to emission reduction [18] and the discharge limits [19]). The legal management framework adopted for the Venice lagoon and its catchment basin anticipated the '*combined approach*' requested by the WFD (Art. 10) and the new approach to dangerous, priority and priority hazardous substances.

It is important to point out that the regulation for quality standards [15] regarding newly authorised industrial discharges, bans any further release of five classes of substances into the Venice lagoon and its catchment area (PAHs, dioxins, PCBs, tributyltin, organochlorine pesticides), to which 5 other dangerous substances (As, Cd, Hg, Pb, CN^-) was added [16]. The cited regulation [15] fixed specific EQSs for the freshwater flowing into the Venice lagoon (see Table 3). The regulation on discharge limit values [19] also established the analytical techniques to be used for monitoring, together with their attainable LODs.

In this paper, 22 industrial activities which directly discharge into surface waters were considered. Seventy-nine types of discharges were identified, of which 12 were from WWTPs. Forty-one surface water monitoring stations were studied (Figure 2).

2. Materials and methods

2.1. *The monitoring of selected pollutants in the Venice lagoon catchment area*

The approach used by the Veneto Regional Environmental Prevention and Protection Agency (ARPAV, which is the institutional body responsible for environmental monitoring and control in the Veneto Region in Northern Italy) in the experimental monitoring of pollutants has been the following: the industrial discharges and municipal wastewater treatment plant effluents were controlled by analysing the same parameters as those monitored in surface waters. Concurrently, the industrial production cycles present in the area were examined in order to predict the potential occurrence of PSs and PHSs.

The priority (P) and priority hazardous (PH) substances contained in the Italian national list (decree n. 367/2003, modified by decree n. 152/2006) and considered in this paper were: cadmium (PH), mercury (PH), chromium, nickel (P), lead (P), tributyltin (PH), alachlor (P), atrazine (P), benzene (P), chlorpyrifos (P), 1,2-dichloroethane (P), endosulfan (P), hexachlorobenzene (PH), hexachlorobutadiene (PH), hexachlorocyclohexane (α, β, γ isomers) (PH), pentachlorobenzene (PH), total PAH (PH), benzo(a)pirene (PH), benzo(b)fluoranthene (PH), benzo(g,h,i)perilene (PH), benzo(k)fluoranthene (PH), indeno(1,2,3-cd)pirene (PH), trichlorobenzene and chloroform (P).

The chemical analyses, carried out during the period from September 1998 to March 2003, regarding industrial discharges and the WWTPs treatment of industrial wastewaters in the Venice lagoon, were provided by the ARPAV laboratory service of Venice.

The overall data set elaborated for the purpose of this study comprised concentrations of the above listed P and PH substances in 848 samples taken from final industrial discharges, 228 samples from final mixed (industrial and municipal) discharges, and 6478 samples of surface waters. The overall number of Ps and PHs substances analysed, compared with the overall number reported in the national list, are shown in Table 2, while Table 4 reports the overall number of industrial, municipal, and surface water samples in which the inorganic and organic pollutants were analysed.

2.2. *Conceptual framework for the integration of the DPSIR model with the Environmental Risk Assessment procedure*

The DPSIR model, proposed by the European Environmental Agency [5], was derived from the simpler *Pressure-State-Responses* model [20,21]. The DPSIR model illustrates the complexity of socio-environmental interactions. It also allows for the calculation of the relative possibility of reaching the objectives of an intervention program [22].

The *Environmental Risk Assessment* (ERA) is the process which evaluates the likelihood of adverse effects to human health and the ecology which may occur, or are occurring, as a result of exposure to one or more of the stressors. In more detail, the ERA concerns the examination of the risks resulting from hazards in the environment that threaten ecosystems, plants, animals and people. It includes the *Health Risk Assessment* to humans and the *Ecological Risk Assessment*. To be more precise, the *Ecological Risk Assessment* is a procedure aimed at the organisation and analysis of data, information, assumptions and uncertainties, in order to evaluate the likelihood of adverse ecological occurrences [14,23,24]. These risk assessment and management techniques are used more and more as decision-making tools for: (a) drawing up regulations; (b) providing a basis for site-specific decisions; (c) ranking environmental risks; and (d) comparing risks.

On this basis, the ERA has become useful for the planning and management of land use and for the definition of environmental monitoring plans. Two tiers are normally employed when applying the ERA method: (i) a screening assessment; and (ii) a definitive assessment [25]. The screening assessments are intended to narrow the scope of the subsequent assessments by screening out the chemicals, media, or routes of exposure that are not recognised hazards. The ERA is used for screening as well as site-specific analysis. The screening analysis is not site-specific, but can give useful information about potential risks to ecosystems.

The proposed methodological approach concerning the integration of the DPSIR with the ERA is shown in Figure 3. This scheme must be applied at both national and local levels (river catchments) so that the following stages of analysis can be met:

(1) the *Screening Risk Assessment*, which defines the national lists of priority and priority hazardous substances;

Table 4. Data set of analytical data used in this study.

Substances	Number of analysed samples: Municipal discharges	Number of analysed samples: Industrial discharges	Number of analysed samples: Surface waters
Inorganic pollutants	228	848	1238
Organic pollutants	153	786	6478

(2) the *Site-specific Risk Assessment*, which is used, in particular, to define basin specific pollutants and hot spots (impact assessments);
(3) the *Risk Management Assessment*, which is used to define the acceptable and unacceptable risks involved, and to subsequently support specific policies and actions to be taken.

The ERA screening procedure permits the identification of the substances to be monitored. It can then be used for the formulation of the EQSs, while the assessment–management framework is provided by the DPSIR model. The novelty of this approach when compared with the 'old one' is evident here: i.e. the priority substances are identified and their EQSs are fixed at a European level. In regards to the other potential priority substances and dangerous substances in the list of main pollutants, the Member States must arrive at the definition of the EQSs by means of the Risk Assessment procedure. The novelty of this new approach is that the list is no longer fixed but remains open, and can be developed at both national and local level (river basins) with the support of a management tool.

A clear advantage in the integration of the DPSIR and the ERA is represented by the linking of inventories, monitoring and intervention measures (policies and actions) [26,27]. With reference to the management model in Figure 3, this paper focuses on the ERA screening needed for the identification of the risks posed by some dangerous and priority substances. The analysis presented in this paper must be considered as a preliminary initiative, which indicates what types of additional investigations should be carried out.

2.3. *The classification of river water quality, applied to waste and surface water, using the ERA approach*

All the chemical substances analysed were determined as dissolved species (in accordance with the Italian regulations) following a filtration process (0.45 μm filter) used for the surface waters, and after a two hour decantation period for the discharges. The collected data used in the study were handled by ARPAV and for the implementation of the special regulations concerning Venice and its lagoon (i.e. the decree dated 30/07/1999 [19] relating to discharge control and the decree dated 23/04/1998 [15] concerning environmental quality standards).

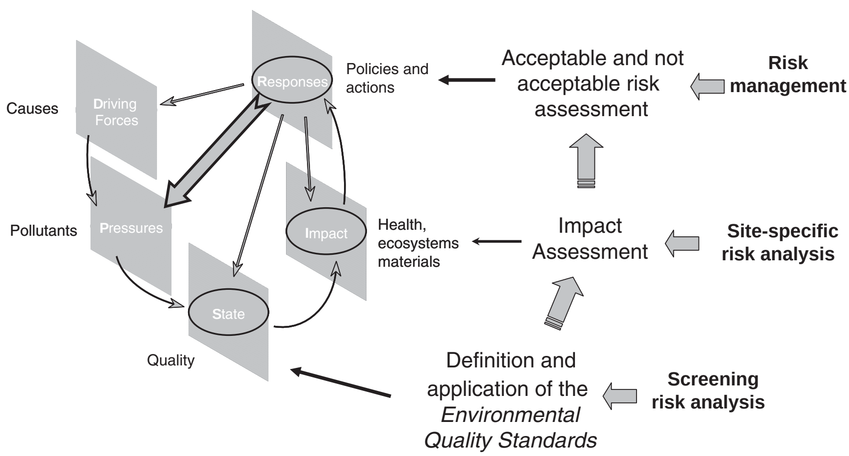

Figure 3. Proposed conceptual framework – role of environmental risk assessment in the DPSIR environmental management model regarding the monitoring and control of priority substances.

Table 3 shows a comparison between the water quality standards established by the Italian regulations (the Italian national and local lists) and the entire list of the European P and PH substances, the limit values for discharges and the limits of detection (the LOD was in accordance with Hubaux-Vos [28,29]). The above values were obtained, for the purposes of this investigation, from the ARPAV Venice Laboratory Service for the monitoring of wastewater and surface waters. These limits have already been established in the Venice lagoon and illustrate the main issues associated with the control of priority substances. In addition, Table 3 presents the analytical techniques adopted and the LODs.

Surprisingly, out of a total of 160 substances in the Italian National list, the EQSs for just about 60 priority substances were actually established (decree n. 367/2003, modified by decree n. 152/2006). These standards were fixed using the values available at European level (i.e. the 'daughter directives' in Directive 76/464/EEC), and a highly conservative approach was therefore used for their establishment. Regarding the Venice lagoon, where there is no existing value system concerning the rivers in the Venice lagoon catchment area (i.e. a guide value), the official value for each parameter, given in the local list [15], is reported in Table 3.

The EQSs and discharge limit values for the Venice Lagoon and its catchment area, as well as the acceptable loads for the lagoon, were defined by the National Institute for Health (the ISS) and by the National Research Council Water Institute (the IRSA-CNR) [30,31]. When these studies were carried out, the previously established data concerning the characterisation of the existing discharges into the Venice lagoon catchment area, the water quality data characterisation, the estimated loads and the defined water quality objectives were taken into consideration, in order to guarantee the maintenance of the capacity of the auto-depuration system and the existing biological community (political objectives).

The local list of parameters, together with the EQSs for the Venice lagoon catchment basin were developed on the basis of a conservative risk analysis model concerning the protection of the entire ecosystem. A comprehensive approach was taken regarding the lagoon, based on the mass balance for each pollutant, estimated by taking into account the inflow and elimination processes, and by studying a complete mixing model and the pollutant loads discharged over the past decades. Two limits for the quality objectives were defined: a lower limit, corresponding to the background level and an upper limit, defined on the basis of a toxicity and eco-toxicity assessment and the use of the matrix (i.e. water quality, sediments and fish/mussels for human consumption).

In this paper, the cumulative distribution of exposure regarding each pollutant (i.e. the cumulative frequency of the observed measurements of contaminants in discharges and in natural waters) was compared with the limit values and the EQSs already in force respectively for discharges and for surface waters. These comparisons were carried out at both national and local (Venice lagoon catchment) level by means of a screening analysis, using cumulative ERA graphs, in order to obtain a preliminary assessment of the *risk-based monitoring* activities. The monitoring results are presented as cumulative curves. The EQSs/limit values were compared with the cumulative frequency, using an ERA screening approach, which had already been adopted for the sediments in the lagoon of Venice [14] and at international level [32]. The monitoring results were also compared with the LODs achieved.

In this way, the critical parameters can be identified and then adequately monitored, so that intervention measures which reach the quality objective can be proposed. The implementation of the EQSs in the cases of the PSs, the PHSs and dangerous substances will greatly affect both the assessment (especially the monitoring efforts) and the management of natural waters. The ERA screening assessment permits the identification of the high risk substances and sources on which the monitoring plan must be focused, and gives support to the DPSIR model for WFD implementation on taking adequate measures of intervention.

Substances with concentration values higher than the EQS or the discharge limit values represent a potential risk for the aquatic environment. The monitoring of these parameters must be intensified (by means of investigative monitoring, in accordance with the WFD) so that the (sometimes unknown) sources can be identified and adequate measures for the reduction or elimination of the substances of concern can be taken, in accordance with the WFD objectives.

3. Results and discussion

3.1. *ERA screening applied to wastewater and surface waters*

It must be observed (Table 3) that the priority substances mentioned in the regulations concerning the Venice lagoon and its catchment area are fewer than those reported in the Italian national list (decree n. 367/2003, modified by decree n. 152/2006) and that some of them, namely the heavy metals, benzene, toluene, xilene, tetrachloromethane, lindane, atrazine, simazine and the PCBs, have lower EQS than those of the same substances in the national list fixed for 2015.

Figures 4–8 show the cumulative concentration frequency plots for the priority substances examined, which are systematically, or very frequently, found in industrial and municipal discharges (i.e. lead, nickel and chloroform – Figures 4–6) and in surface waters (i.e. lead and chloroform – Figures 7 and 8). The same type of analysis was carried out with regard to As, Cr, Cu, Zn, and phenols, but has not been included here so as to simplify the explanation.

The remaining priority substances examined in this study (i.e. cadmium, mercury, tributyltin, alachlor, atrazine, benzene, chlorpyrifos, 1,2-dichloroethane, endosulfan, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane (α, β, γ isomers), pentachlorobenzene, the total PAH, benzo(a)pirene, benzo(b)fluoranthene, benzo(g,h,i)perilene, benzo(k)fluoranthene, indeno(1,2,3-cd)pirene, trichlorobenzene, and PCBs) were recorded below the LOD and then only occasionally either in discharges or in surface waters.

In regards to the As, Pb, Cr, Ni, Cu, Zn, chlorofom and phenol parameters, the assessment of the available data set indicates that municipal discharges do not represent a potential risk, as in general their concentration values are usually lower than the concentration limit values.

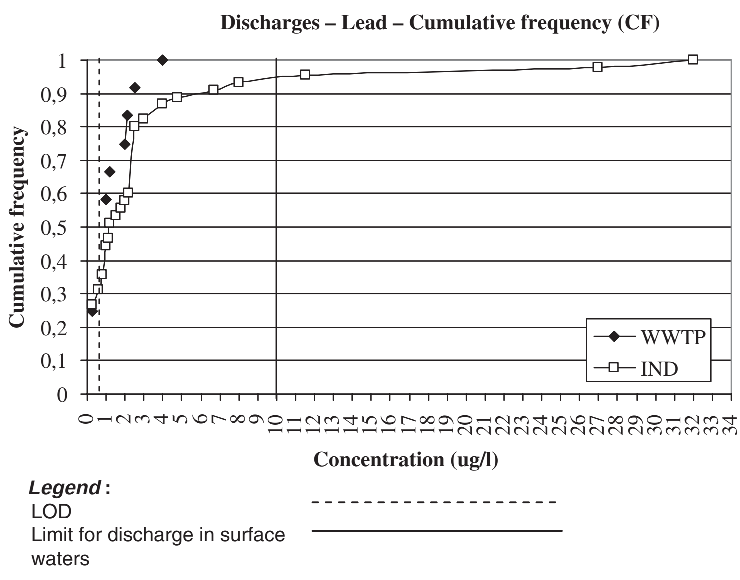

Figure 4. Screening risk assessment for lead: cumulative distribution of exposure versus discharge limit values (WWTP: wastewater treatment plant discharges; IND: industrial discharges).

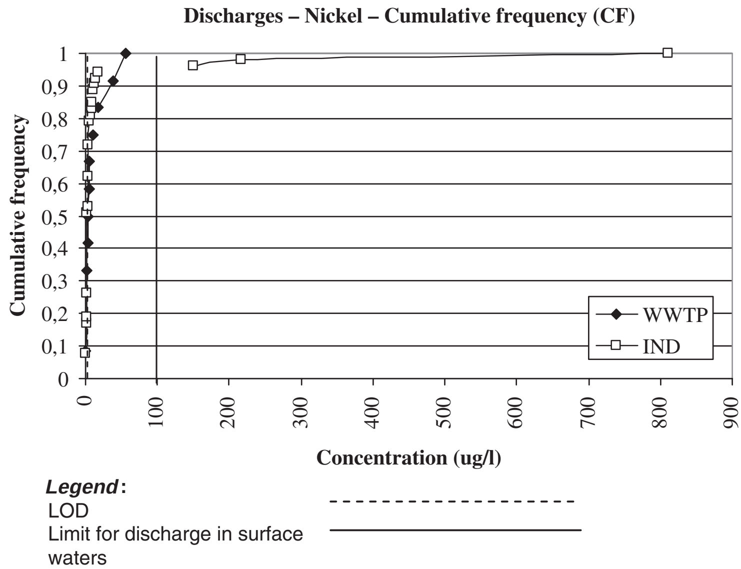

Figure 5. Screening risk assessment for nickel: cumulative distribution of exposure versus discharge limit values (WWTP: wastewater treatment plant discharges; IND: industrial discharges).

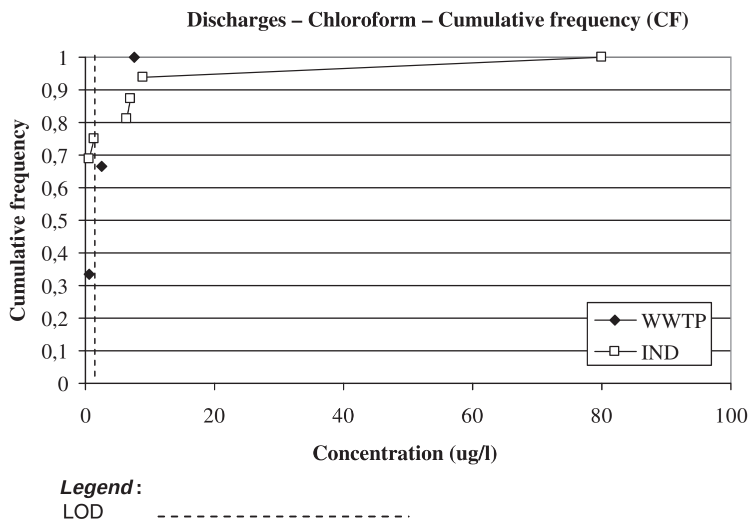

Figure 6. Screening risk assessment for chloroform: cumulative distribution of exposure versus discharge limit values (WWTP: wastewater treatment plants discharges; IND: industrial discharges).

Contrarily, a significant potential risk is represented by the industrial discharges, mainly because they contain As, Pb, Zn, Cr, Ni, and Cu. Moreover, the ERA screening analysis indicated that the substances which frequently exceeded the limit values and were therefore a potential risk for ecosystems, were Pb and Zn. The available data also suggest that the organic priority substances with concentrations higher than the LODs (e.g. chloroform and phenols) do not appear to pose a potential risk, in terms of the existing limit values for discharges.

For example, the cumulative distribution curves for As, Pb and chloroform in surface waters, shown in Figures 7 and 8, refer to the 2008 and 2015 EQSs fixed by the national regulations (Table 3) and to the LODs and EQSs fixed by the regulations for the Venice lagoon and its

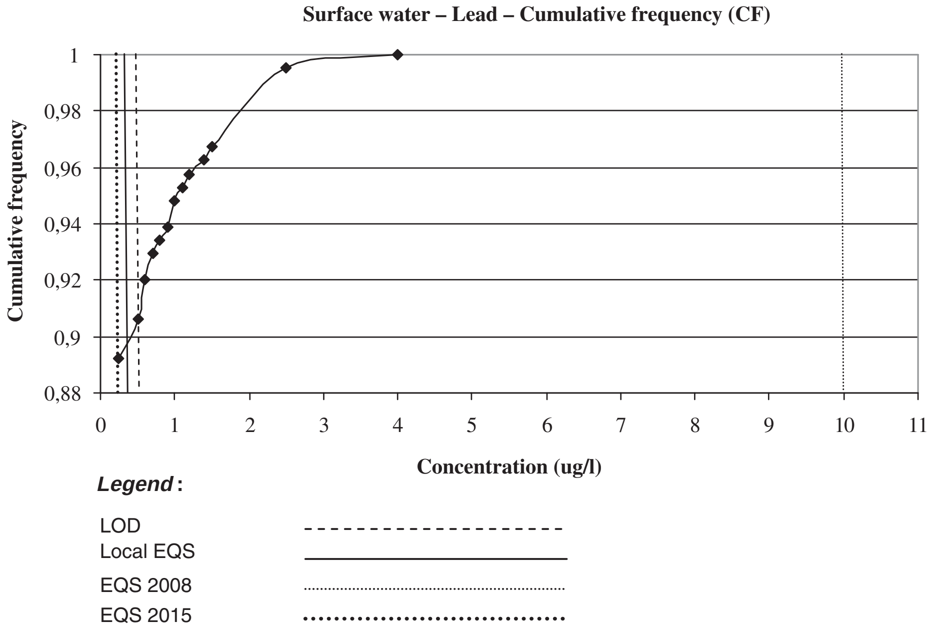

Figure 7. Screening risk assessment for lead: cumulative distribution of exposure versus water quality standards.

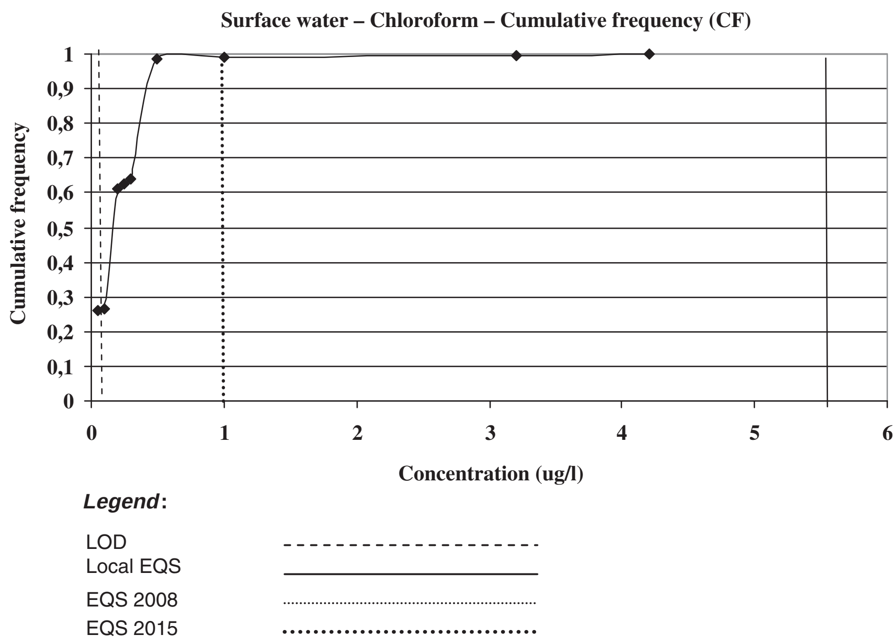

Figure 8. Screening risk assessment for chloroform: cumulative distribution of exposure versus water quality standards.

catchment area (i.e. the local EQSs). With reference to the local EQSs, the potential risk for ecosystems posed by As, Pb, and chloroform is high. While the concentrations of most of the other priority substances examined are lower than the LODs or than the most restrictive local/national EQSs, for some substances, the achievable LODs were not low enough to fix their EQSs and thus to evaluate their chemical status (as can be seen in Table 3).

Although the reference to the LODs, which merely indicates the presence/absence of a substance, may be questionable, it offers a useful indication of the achievability of EQS over a reasonable time period. When Table 3 is scrutinised, it can be seen that the EQSs to be reached by the year 2008 (i.e. 2008 EQSs) regarding the inorganic and organic PSs and PHSs were achieved using the LODs based on the already existing methods, and the analytical techniques reported in Table 3. An exception to the latter is the case of metallorganic Tributyltin (a LOD of 0.03 μg/l compared with an EQS of 0.001 μg/l in 2008) and also the case of the individual Policyclic Aromatic Hydrocarbons (i.e. benzo(a)pirene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perilene). It should also be noted that tributylcation, some of the Policyclic Aromatic Hydrocarbons (i.e. antracene, fluoranthene, naphthalene), di(2-ethylhexyl)phthalate, pentachlorophenol, α-endosulfan, simazine, clorfenvinphos, trifularin, chloroalkanes, the total brominated dephenylethers and the alkylphenols (i.e. nonylphenols and octylphenols) have not been examined due to a lack of standardised methods and available analytical techniques. When the 2015 EQSs are compared with the currently attainable LODs, it follows that most PSs and PHSs contained in the European list of priority pollutants are too distant to be measured in natural waters using the current officially, or internationally, validated analytical methods.

The above considerations seem to suggest that the WFD implementation requires a greater analytical effort, since the concentration value for each EQS should be sufficient to meet the limit of quantification (LOQ), which is normally a factor of 5 to 10 higher than the LOD. It follows that the LOD in table 3 should be replaced by the LOQ as soon as possible; i.e. it should be increased by a factor of 5 to 10, in order to ensure a reliable monitoring of the EQSs. The optimisation of the existing methods, and the development of new methods, should be put into practice for a large number of priority substances definitively, in view of the monitoring activities demanded by the WFD by the year 2015.

4. Conclusions

According to the results from this study, a comprehensive DPSIR and risk-based approach to design the monitoring of water bodies and the management of the pressure sources at the river basin level requires: a thorough knowledge of the dangerous and priority substances used in industrial production cycles; the control of these substances in industrial and municipal effluent wastewaters (inventory analysis); the monitoring of concerned water bodies; the quantification of Environmental Quality Standards (EQSs) and discharge limits by using the *Environmental Risk Assessment*.

Pending the complete implementation of the WFD, the authors would like to suggest the following steps to be taken:

- the identification, at the river basin level, of the additional priority substances, as required by the WFD;
- the assessment, on the basis of the existing potential sources, of the monitoring data, the toxicological information and which substances may pose a significant risk to aquatic organisms and human health;
- the implementation of the environmental monitoring, following the setting up of adequate analytical methods suitable for coping with enforced EQSs;
- the verification of the question as to whether concentrations of specific substances, or mixtures of substances, which exceed the proposed EQSs, might cause a significant risk to the environment or not.

The EQS concentration values, to be fixed for the priority substances by the year 2015, require the development of analytical methods which are not yet available or, where available, are not sufficiently sensitive and/or selective. The decrease in the limit of the current methods of detection-LOD by a factor of 10–100 for natural waters can be accomplished by means of effective sample pre-concentration/clean-up methods, coupled with detection systems based on low or high resolution mass spectrometry.

The case study of the Venice lagoon catchment basin has been presented and discussed in this paper, together with the integration of the screening ERA with the DPSIR model. In regards to civil WWTPs, no risks were observed concerning discharges, whilst regarding industrial discharges, potential risks were posed by the As, Pb, Zn, Cr, Ni and Cu parameters.

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