

## **END USER'S VIEW : STATE OF THE ART, IDENTIFICATION AND PRIORITISATION OF NEEDS.**

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### **1. Legislation references - the situation in Italy**

As far as the monitoring of water quality is concerned, one particular law constitutes the benchmark for the Italian industry - law n° 319 emanated on May 10th, 1976 ("Regulations for the protection of waters from pollution" ; this law is commonly known as the 'Merli law' taken from the name of the parliamentary member who proposed and obtained approval for the bill) .[ 1]

The Merli law has, amongst others, the following purposes :

- the regulation of any type of waste water, public or private, direct or indirect, in all waters - surface and groundwater, inland and at sea, both public and private, in sewers and on land or in the subsoil;
- the formulation of general criteria for the utilisation and discharge of waters in plants ;
- the organisation of public services such as water supply, sewer systems and depuration,
- the drawing up of a general plan for water remediation on a regional basis ;
- the systematic monitoring of qualitative and quantitative data pertaining to water bodies.

This law establishes a single set of regulations, applicable throughout the nation, for discharges based on the definition of acceptability limits for these as prescribed in tables A, B and C of the law.

Table A, for example, indicates 51 parameters to be respected in terms of concentration limits. This table relates to the limits set for liquid discharges that industries must respect within the first 3 years of the law being approved.

Table C, on the other hand, contains concentration limits for liquid discharges which are more restrictive. Industries are required to conform to these levels within 6 years following approval of the law (this expiry term has been protracted several times).

During the 1980s, therefore, the entire Italian industry had to conform to the limits set for discharges in these two famous tables.

The Merli law set out, moreover, a system of authorisations and monitoring activity to be effected on discharges. "The measuring of discharge shall be performed immediately before the point of immission into the receiving body..."

The law prescribed, amongst other things, a specific controlling authority within the production plants. "The controlling authority is empowered to carry out those inspections,

within the plant, which it considers necessary to ascertain any conditions which give rise to the formation of discharges”.

The controlling authority can order that partial discharges containing total toxic metals and non-metals (As - Cd - Cr(VI) - Cu - Hg - Ni - Pb - Se - Zn) undergo special treatment before they run into the general discharge.

With reference to analytical determinations, the Merli law requires that they be effected on an average sample, taken during an interval of not less than three hours.

“The analysis and sampling methods adopted in the determination of parameters are those described in the volume ‘Metodi analitici per le acque’ (Water analysis methods) published by the The Institute of Water Research of the National Council of Research in Rome (CNR)”.

Without going into the details of the complex history of the Merli law and its subsequent modifications and extensions, it is possible to say that this law has been considered as particularly strict, so much so that Italy is exonerated from adopting the European directives on waters.

Only following a sentence issued by the Court of Justice in Luxembourg (dated 28 February 1991) did Italy find itself forced to adopt, from 1992, numerous European directives [previously not considered] under two legislative decrees.

(Legislative decree n° 132 dated 27 January 1992 “ Implementation of directive 80/68/EEC concerning the protection of groundwaters from pollution caused by certain hazardous substances” [2]

Legislative decree n° 133 dated 27 January 1992 “ Implementation of directives 76/464/EEC, 82/176/EEC, 83/513/EEC, 84/156/EEC, 88/491/EEC, 88/437/EEC, 90/415/EEC on the subject of industrial discharges of hazardous substances in waters ”) [3]

These norms gave way to a major review of the requirements established by the Merli law in the matter industrial discharges. From the definition of maximum values for pollutants contained in discharges, applicable throughout the Italian state and for all plants, new specific value limits were set on the basis of each production process (the so-called best available technology) in order to proceed to the next stage which consists of a general system of authorisation that also evaluates the quality of the receiving water body.

Thus, since 1992, Italian legislation on waters has taken a decisive turn towards alignment with European directives. This process of alignment is not fully completed.

## **2. Design evolution of industrial plants in reference to the norms on protection of groundwaters and industrial plant discharges**

The legislative decree n° 132 issued 27 January 1992, which incorporates into Italian legislation the EEC directive n° 80/68 regarding the protection of groundwaters from pollution provoked by certain hazardous substances, imposes particularly stringent constraints on industrial plant design engineers.

In order to obtain authorisation to discharge industrial waste into water bodies it is necessary to provide a documented report which demonstrates that during the design stage everything has been done to ensure that there is no risk of contaminating the groundwaters with substances specified in lists I and II of the attachments contained in directive 80/68/EEC, i.e.

those substances included in the black list and in the grey list of the directive n° 76/464 , which is the source for all European directives on waters.

The system of authorisation, defined in the abovenamed legislative decree, requires that all industrial plants present a geological report, prepared by a qualified geologist, on the hydrogeological conditions of the area concerned, possible depuration capacity of the soil and subsoil, risk of pollution and alteration in the quality of groundwaters.

Similarly, legislative decree n° 133 issued 27 January 1992, which incorporates into Italian legislation 7 EEC directives on the question of industrial discharge of hazardous substances into water bodies, also defines a system of authorisation which involves, with reference to those substances included in the abovementioned black list and grey list, the following :

- the indication of the production capacity of the individual plant;
- the hourly water requirement of the specific production process;
- the possible discharge flow measurement system, where requested;
- the technical equipment employed in the production process and in the waste discharge system to reduce pollution;
- the depuration systems utilised to ensure that emission regulations are observed.

It is important to note, with regard to the Italian situation, that the obligations imposed by the incorporation of the EEC directive, since 1992, have forced industries to carry out extensive analyses and studies in all areas concerning the process fluids used and waste liquids produced. In the large industrial plants the provisions of this law have involved a total reconsideration of the design aspects of all the water cycle.

If one takes, for example, a large ENEL coal-fired power station as a reference the final unified project would take into consideration seven different waste liquid qualities and propose a separate circuit system for each :

- Rainwaters
- Sanitary waters
- Oily water
- Acid and/or Alkaline water
- Waters deriving from coal deposits
- Desulphurisation effluent
- Denitrification effluent

In addition to these seven process waste collection systems it is necessary to consider the principal condenser water cooling system, in which monitoring at discharge of any residual quantity of chlorine compound added for antifouling is often called for .

These references to the current legislation and effects on the design of waste water systems in industrial plants have been made in order to convey the spectrum of problems which Italian industrial plants have been facing over the last few years , while providing a backdrop for the subject of this paper i.e. the monitoring of water quality.

With these more advanced waste collection system configurations, new forms of waste water management become feasible. It is possible to carry out temporary storage of some wastes so optimising their treatment and reutilization .

The link between various wastes before discharge can be configured in different ways (in series or in parallel). There are technical opportunities (Pinch analysis) which enable an optimisation of the entire plant waste treatment process. Given such an articulated plant system a number of new possibilities arise for the recovery and reutilization of waters (zero discharge).

The problems described above call for an in-plant implementation of waste water measuring instruments capable of monitoring the evolution of the waste water characteristics within the system process (Monitoring of intermediate waste waters).

### **3. State of the art of water quality monitoring**

#### *3.1. Application fields*

In terms of the industrial system, it can be said that the field of application in monitoring of water quality in Italy is defined by the demands imposed the law at the point of discharge (monitoring of output).

In reality the evolution of legislation on the issue, reduction of hydric resources, pollution of groundwaters and increasing supply costs all concur to make industry not only evaluate the quality of discharges but also the quality of incoming water used in the plant.

From this point of view the situation in Italy differs greatly from region to region as a result of its complex geographic relief .

Industrial plants receive their water from groundwater, rivers, lakes and seas. The monitoring of incoming water (monitoring of input) to the plant acquires, in reality, the same importance as monitoring of discharges .

This point leads to the consideration of natural hydric bodies in a new environmental light.

There is an ever increasing number of projects which feature the productive utilisation of the large masses of water contained in the great lakes located in the North of Italy (Lake Maggiore, Lake Como, Lake Garda).

The monitoring of water quality in these lakes constitutes a scientific and environmental issue of great interest which dates back many years with considerable research, especially in the field of water monitoring.

Reference has been made to the importance of monitoring within the plant system (monitoring of intermediate waste waters) .This constitutes, predictably, an application field currently being developed and implemented primarily in relation to water recycling and reutilization policies (zero discharge)

The topic of groundwater monitoring also lies within the sphere of industrial interest because of both the necessity to extract water from existing wells in the plant and to prevent, or control, contamination of the substrata which has taken place during the life of the plant. The dislocation of industrial production residues as a consequence of precipitation has given rise to

the phenomena of leaching and substrata contamination. Industrial companies are often involved in problems of contaminated site remediation . Faced with such events, the health authorities often require the remediation of the site and verification of the results through long term monitoring of the situation (monitoring of contaminated sites).

The same principles apply to sediments that collect in rivers or lakes in the vicinity of industrial discharge outlets and have a long history of pollution phenomena. In these cases monitoring activity also becomes necessary (monitoring of sediment). (see annex 1)

Developing studies and research, monitoring instruments for the large masses of water in the great lakes is also of interest to the Italian industry, which sees in these areas an important hydric resource that is available at certain conditions.

Equally important are the large rivers to which the Italian industry, following law n°183 (1989) under which “hydric basin authorities” were set up, looks with interest in terms of monitoring the water flows, considering these water masses as valuable resources to preserve and prevent from pollution.

### *3. 2. Measurement aim*

The measuring aims in the activities indicated above are, from an industrial point of view, first and foremost observance of the law and compliance with requests from controlling authorities (monitoring of output).

The economic necessity to optimise the management of wastes forms a second aim (monitoring of input, monitoring of intermediate waste water).

The need for environmental control, often imposed on industry by health authorities, constitutes a commitment which requires the development of monitoring activities that accompany remediation activities in cases where the environmental situation is endangered (monitoring of groundwater, monitoring of contaminated sites, monitoring of sediments)

### *3. 3. Measured parameters and considered concepts*

The industrial measurement needs illustrated above necessitate the development of diverse instrumentation.

#### *3. 3. 1. Monitoring of output*

As far as the first need is concerned i.e. waste control (monitoring of output), the ranges to be measured are substantially those comprised within the European Directive lists (black and grey lists contained in directive 76/464 and attachment I of Directive 80/778).

The legal control of wastes requires considerable reliability from the instrumentation utilised in continuous monitoring .

The discharge of cooling water from industrial plants such as Thermoelectric Power Stations can create ecological problems.

For example flow of cooling water (80 m<sup>3</sup>/sec) from the Porto Tolle (4x660 MW) Thermoelectric Power Plant can be taken and discharged in River Po, the Adriatic sea or even the nearby Lagoons (see Annex 2).

Monitoring of water and ecological conditions must be studied with care and assessed for environmental impact.

The study of ecological impact calls for the development of many research lines (see Annex 3).

The quality of water is only one the the many aspects to be considered.

Monitoring activity can be extended to an entire river tract. [4] [5]

That is the case for the River Po (see Annex 4) where eight Thermoelectric Power Plants, located along the River, make it necessary to create a network of continuous monitoring of water quality (dissolved O<sub>2</sub>, Ph, conductivity, turbidity, temperature) (see Annex 4).

### 3. 3. 2. Monitoring of intermediate waste waters

The requirements of different industries vary greatly . Briefly, it can be said that it is fundamental to develop instrumentation able to monitor the result of the principal depuration treatment processes utilised in industry.

These include:

- sedimentation processes
- clarification processes
- precipitation processes
- defiltration processes
- disinfecting processes
- biological deposit elimination processes

### 3. 3. 3. Monitoring of groundwater

In some situations it becomes necessary to define programs for the monitoring of groundwaters subject to risk of contamination.

It is important to develop measurement techniques capable of providing reliable instruments and measurements which are easily installed for long term measuring campaigns . Further development of sensors, other than those for traditional parameters (temperature, pH, conductivity, dissolved oxygen, Redox potential, turbidity), should include those relative to the list of substances contained in the attachments of the abovementioned European Directives on water quality. The configurations of measurement and performance must be adapted to the monitoring procedures referred to autonomous units with reduced maintenance needs, long operation times and continuous data recording.

Groundwater monitoring and characterisation activities have resulted in the construction of penetrometric units capable of collecting soil, interstitial air and water samples, at the same time. (see Annex 6).

With reference to water, it is possible to measure Ph, Redox potential, conductivity, dissolved O<sub>2</sub>, temperature and pressure).

Many other parameters could be measured in this manner utilising the miniaturisation of the measurement flow cell.

Mobile laboratories can utilize this penetrometric unit to characterise contaminated sites “in situ”.

### 3. 3. 4. Monitoring of sediment

Previous experience leads us to propose and sustain the development of direct measuring techniques capable of supplying information on the condition of the sediment present on sea and lake beds which have been subjected to pollution.

Measurements concerning the water-sediment interface must have a high spatial elevation resolution (millimetric) given the need to calculate strong gradients . They must also cover a sediment depth which is representative and variable according to the parameter measured.

The water-sediment interface is a key site for all the transformation processes that take place within the sediment ; it also acts as the exchange point between the sediment system, interstitial waters and/or depth waters (nitrification/denitrification, sulphate reduction and sulphur precipitation, phosphate and heavy metal adsorption/desorption, molecular diffusion flows from and to sediment etc.).

The following parameters, amongst others, are indicated for measurement :

- dissolved oxygen
- pH
- Redox potential
- sulphurs
- conductivity
- ammonia
- nitrates
- hydrocarbons

Each of the parameters listed above, along with the relative sensors, presents a different measuring and operating complexity.

Whatever the case, all concern sensors of limited dimensions (from about 10 to 5000 micrometers) which are placed in the sediment at depths which vary according to the sensor response time and at depths beyond which any information acquired is considered to be of secondary importance. (see annex 7)

### 3. 3. 5. Monitoring of contaminated sites

The issue of monitoring of contaminated sites is one of great interest to industry.

Work in this area includes the characterisation of sites using mobile laboratories that can supply rapid responses to questions of risk assessment connected to the phenomenon of water, soil and air pollution.

In terms of water, account must be taken of this aspect in the development of rapid leachate analyses. The parameters to be considered here are also those listed in the attachments to the earlier mentioned European Directives .

In this case the measuring techniques must provide responses in real time in order to achieve the aim of the measurement campaign and the immediate analyses of the samples taken in the site under evaluation. [4]

It is interesting to develop biosensors, capable of producing fast and low cost "in situ" measurements, for the monitoring of pollution in contaminated water.

An immunochemical biosensor for the determination of PCB concentration in contaminated water is currently under development within the terms of a project defined by the Environment Programme founded by the European Union. (contract n° eV5V CT - 94 - 0407 Monitoring of Polychlorinated byphenyls (PCB) in Groundwater through an immunochemical Biosensor with electrochemical detection).

System characteristic include :

- ease and rapidity of performing contaminated soil and water analyses;
- possibility of performing determination "in situ" directly in line with the and without the necessity to treat the samples (see annex 8).

### *3. 4. Present performance*

It is very difficult to express an opinion on the Italian situation in this field.

There is much perplexity on the quality of the instrumentation utilised in continuous monitoring.

The acquisition of measurements, biological growth on instruments, the frequent need to calibrate and reset sensors lead us to conclude that there is still much work to be done in order to implement the quality of information that continuous monitoring systems are able to provide.

### *3. 5. Main drawbacks and limitations*

- Reliability over time of the continuous measurement of water control parameters is a critical factor in many industrial plant situations
- The control methodologies are referred to laboratory analysis methods which involve tests on samples taken from waste waters in a non-continuous manner .
- For reasons of uniformity, existing legislation often only indicates a single method of measurement (measurement of samples taken from the plant and analysed in the laboratory).

These last two points do not encourage the development and acceptance of instrumentation which functions on a continuous basis and inhibits the development of instruments using innovative methodology.

#### **4. Identification and prioritisation of technical and regulatory needs**

Experience has underlined the need for technical norms in the area of industrial wastes which favour the utilisation of continuous instrumentation; conversely the norms tend to restrict the development of new instruments .

A paramount example of the former is the American regulation issued by the ASTM (American Society for Testing and Materials) which, for many of the parameters relative to precisely water and environmental technology, include methods that are specific and exemplified for on-line monitoring .

##### *4. 1. Classical parameters : required performance*

With reference to the classical parameters reported in the attachments to the European Directives on waters, it is proposed that a set of technical regulations be drawn up which promotes on-line monitoring and recognises, furthermore, the possibility of developing new measuring techniques .

On this point the following are considered important in terms of interesting techniques :

- FIA technique (Flow Injection Analysis)
- PSA technique (Potentiometric Stripping Anodic)
- LFA technique (Loop Flow Analysis)

##### *4. 2. New concepts to consider , new parameters to be measured*

The monitoring of groundwaters, contaminated sites and sediments requires the development of new measurement parameters and new instrumentation.

The development of mobile laboratories for surveys of contaminated sites emphasises the importance of creating instrumentation which is able to offer rapid screening of the contaminated situation and facilitate risk assessment of the area in question.

In this case an evaluation of the need to develop biosensors and, more specifically, techniques which can give a global evaluation of toxicity, must be made.

#### **5. Conclusions**

In terms of the situation in Italy, industry's attention to monitoring of water quality is becoming increasingly conditioned by legislation and, more particularly, by the recent integration of European norms on water quality

The authorisation procedures, prescribed by European norms and directives, require declaration of production cycles, their capacity and concentrations. Supervision by health authorities is not only confined to the output discharges from industrial plants but also within the same plant and may even extend to special prescriptions for partial internal discharges.

In relation to the various forms of hydric supply and specifically those being currently developed (supply from hydric basins, rivers, great lakes) it is in the interests of industry to develop continuous water quality monitoring systems for use at the plant inlet. This will enable plants to modify, control and optimise the initial treatment costs of incoming waters and control the phenomenon of sudden pollution of the water supply source .

With reference to past experience acquired in the field of possible applications and implementations for water quality monitoring it is important to extend these to the monitoring of sediments contained in the hydric bodies receiving the industrial discharges and to the monitoring of leachates (leaching of rain waters on the residues) which may be associated to industrial activity.

Industrial production involves the continual flow of wastes and the need for automatic controls and regulation of treatment plants; it is therefore essential to have adequate monitoring instrumentation. The reliability of such instrumentation is an issue of great concern in the industrial field. All new research initiatives are welcomed, as are the funds necessary to develop monitoring measurements and techniques which are highly reliable and applicable to the control and regulation of industrial treatment systems for polluted waters.

The analytical methods indicated in existing legislation and directives must also take into consideration the need for rapid response and privilege techniques and methods capable of providing immediate results.

Examples of future promising techniques are indicated below :

- FIA technique (Flow Injection Analysis)
- PSA technique (Potentiometric Stripping Anodic)
- LFA technique (Loop Flow Analysis)

In terms of new approaches and ideas to be developed in the field of biosensors the following are pertinent to :

- global evaluation of toxicity

The speed of response provided by biosensors deserves careful attention given the foreseeable advantages offered providing that the measurement systems are thoroughly validated and reliable.

In the context of the Standard, Measurements and Testing, financially supported research aimed at obtaining instrumentation capable of supplying reliable results in minimum time should be considered as a route to followed with greater commitment and resources so as to confer a competitive advantage to European industry and improve environmental protection.

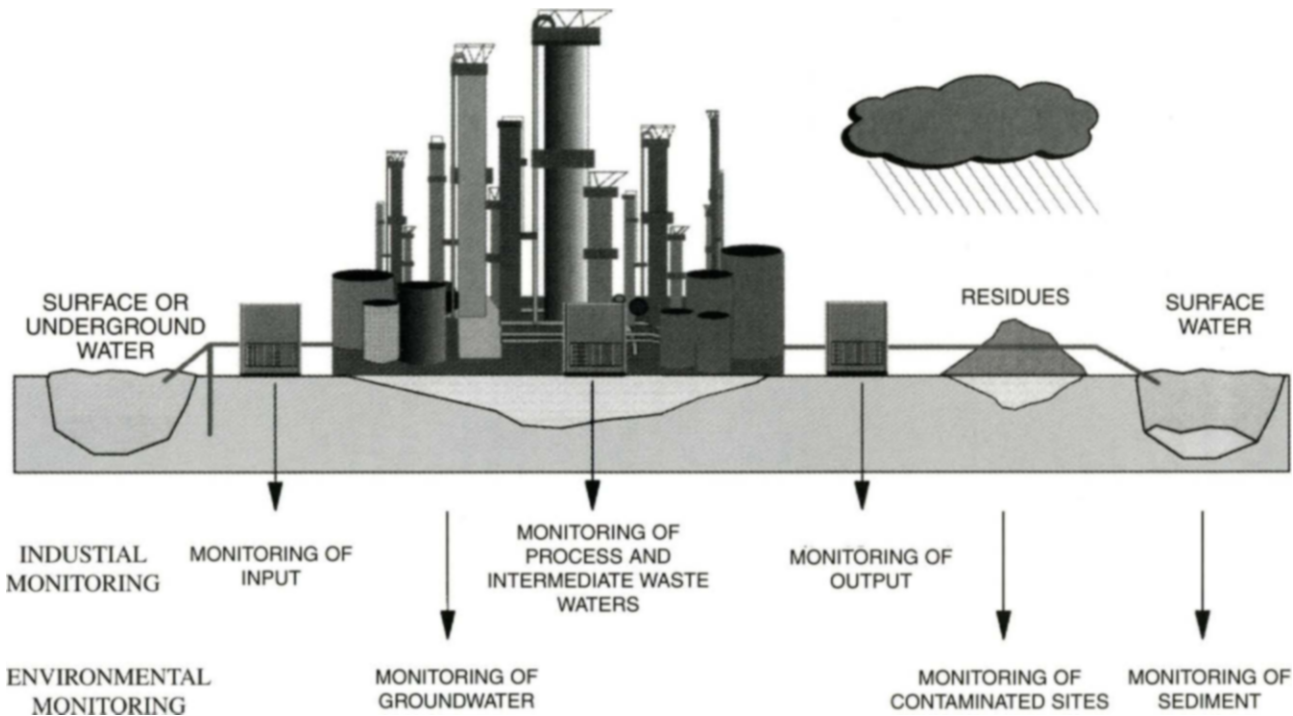
## **6. List of annexes**

- Annex 1 : Monitoring of water quality application fields
- Annex 2 : Porto tolle - thermoelectric power plant (4x660 mw)  
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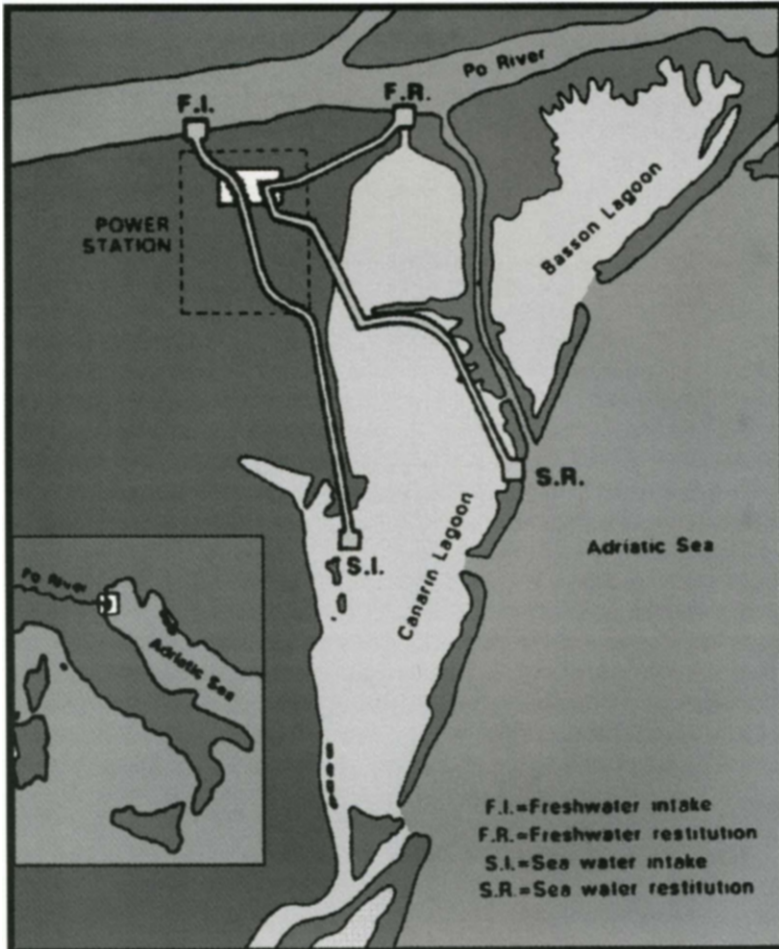
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- [2] "Implementation of Directive 80/68/EEC concerning the protection of groundwaters from pollution caused by certain hazardous substances", Decreto Legislativo n° 132 del 27 gennaio 1992
- [3] Implementation of directives 76/464/EEC, 82/176/EEC, 83/513/EEC, 84/156/EEC, 88/491/EEC, 88/437/EEC, 90/415/EEC on the subject of industrial discharges of hazardous substances in waters", Decreto Legislativo n° 133 del 27 gennaio 1992
- [4] Environmental impact assessment for Italian thermoelectric power plants in coastal zones by R. Ambrogi (ENEL -DSR) and R. Vitali (ENEL -DCO), Bulletin de l'Institut Oceanographique (Monaco - 1992)
- [5] L'influenza del Lambro sul Po., Analisi dei dati della rete di monitoraggio in continuo dell'ENEL, L. Guzzi, G. Bonforte, A. Bozzani, W. Martinotti, ENEL SpA - Centro Ricerca Ambiente e Materiali Milano (IRSA 1996)
- [6] Characterisation and monitoring of industrially contaminated land: The ENEL approach by Giuseppe Frego, Pompilio Caramuscio, Riccardo Elini, Giuseppe Varallo - ENEL SpA-DSR Residue Valorisation and Treatment research Centre - Brindisi, (Network Industrially Contaminated Land in Europe) - Inaugural Meeting of NICOLE, Hannover 21 May 1996.

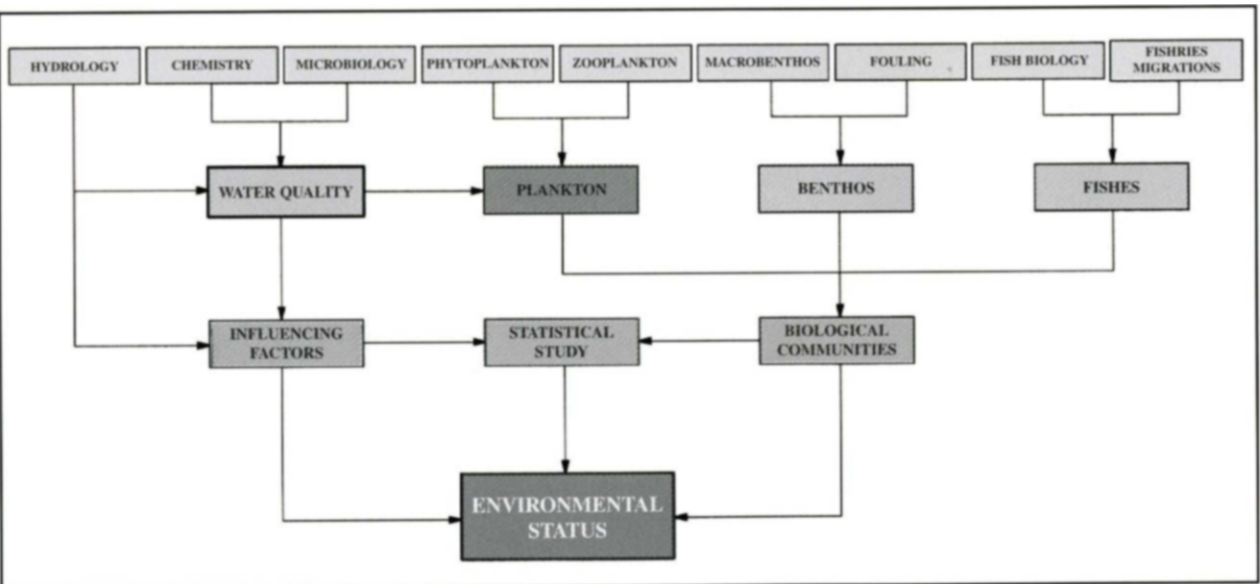
Annex I : Monitoring of water quality application fields



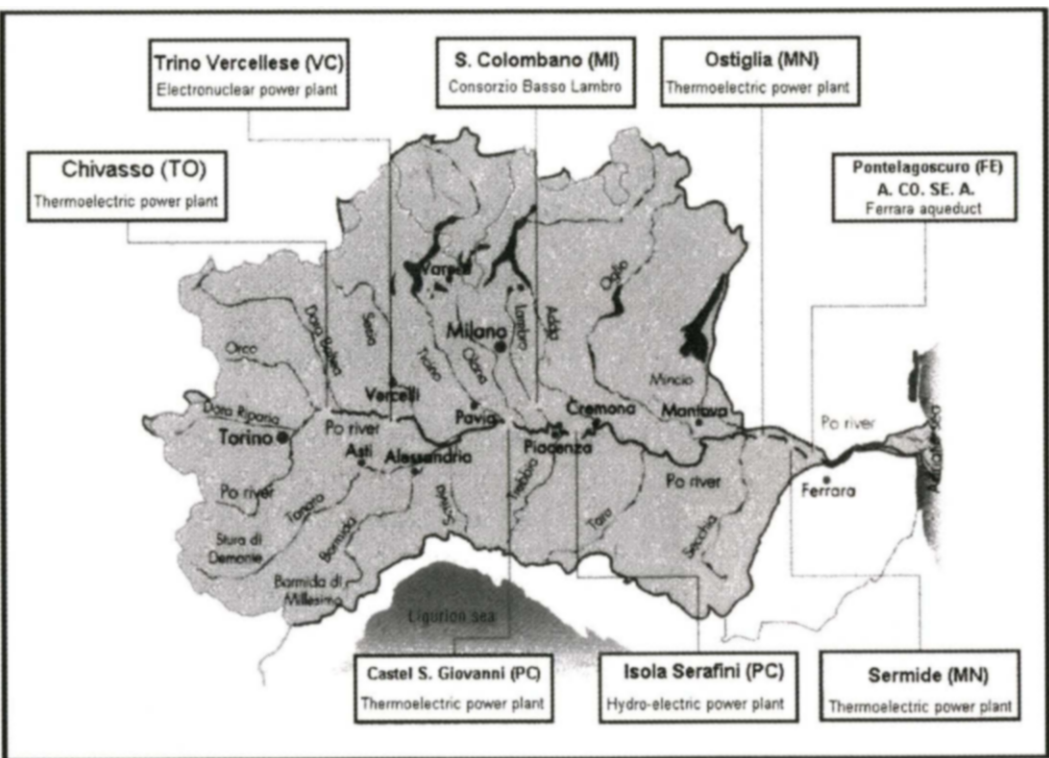
**Annex 2 : Porto tolle - thermoelectric power plant (4x660 mw). Location of the plant and sketch of the cooling circuit**



Annex 3 : The research lines of the environmental impact assessment



**Annex 4 : ENEL/CRAM - network for the continuous monitoring of poriver water quality**

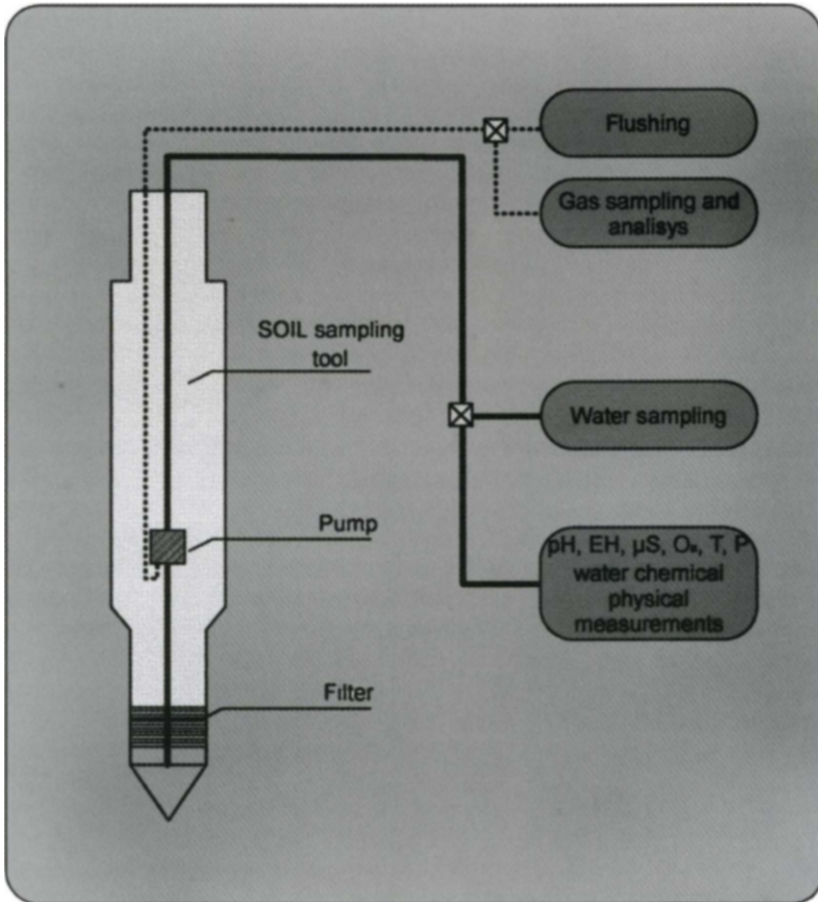


**Annex 5 : Monitoring of output “aqua” automatic unit sensor characteristics**

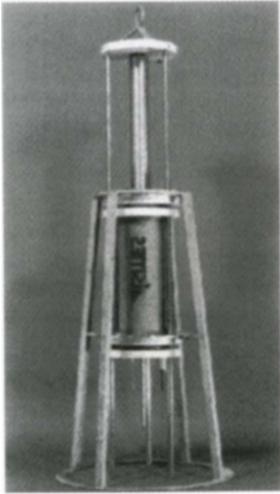
PARAMETER	RANGE
temperature (°C)	-5 ÷ +35
conductivity (ms/cm)	0 ÷ 6
pH	0 ÷ 14
redox (mv)	± 1250
oxygen (mg/l)	0 ÷ 21
turbidity (FTU)	0 ÷ 2/20/200/2000
hydrocarbon fluorescence	0 ÷ 9999.9
well temperature (°C)	0 ÷ +50
piezometric level	0 ÷ 2 (bar)



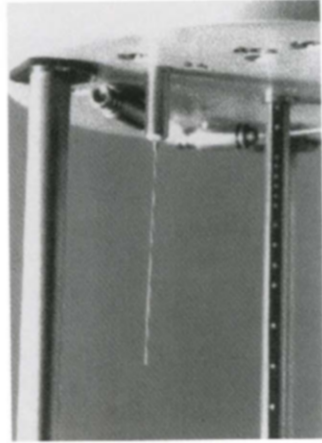
**Annex 6 : Monitoring of groundwater illustration of sampling lines and analyses**



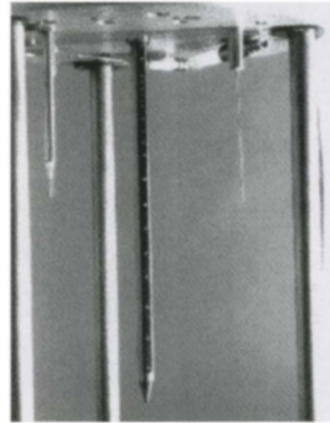
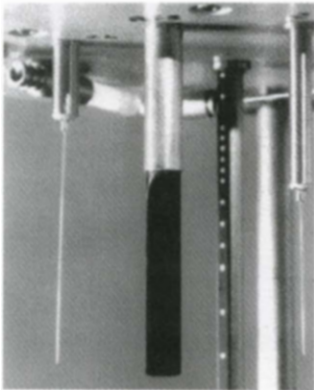
**Annex 7 : Monitoring of sediment**



SWIMP - sediment water interface microprofiler



Sulphide microsensor



### Annex 8 : Monitoring of wastewater

