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REMEDIATION OF CONTAMINATED SITES IN ITALY: STATE OF THE ART OF TECHNOLOGIES AND PLANNING & DESIGN CRITERIA

MAURO MAJONE(*), GIOVANNI PIETRO BERETTA(**), LUCA RAFFAELLI(***), LOREDANA MUSMECI(****) & GIUSEPPE MININNI(*****)

(*) Dipartimento di Chimica, Università "La Sapienza", Roma, mauro.majone@uniroma1.it
(**) Dipartimento di Scienze della Terra "Ardito Desio", Università degli studi di Milano, Milano
(***) Servizio Bonifiche Siti Contaminati, Provincia di Milano, Milano
(****) Istituto Superiore di Sanità, Dipartimento Ambiente e Prevenzione Primaria, Roma
(*****) Istituto di Ricerca sulle Acque, CNR, Roma

INTRODUCTION

Remediation of contaminated sites in Italy has been so far governed by the so-called Ronchi Decree (Ministerial Decree 22/97) and by the subsequent Ministerial Decree 471/99, which laid down detailed procedural and technical provisions. Most of the site remediation projects conducted in Italy have fallen under the scope of the above Decrees.

This legislation was recently revised by Legislative Decree no. 152 of 3 Apr. 2006 (hereafter called "Decree 152/2006"), consolidating and superseding all previous laws and regulations on environmental matters (including general legislation on water protection, namely Legislative Decree no. 152 of 11 May 1999). On the other hand, Decree 152/2006, including provisions on remediation of contaminated sites, is already being overhauled. Against this background, it is useful to make a critical analysis of the seven years of application of the prior legislation (Ministerial Decree 471/99), in order to derive suggestions for the more technical aspects of the ongoing revision.

The following analysis considers both remediation and emergency containment of contaminated groundwater and soil, focusing on the interaction between the legislative-regulatory framework and the consequent technological choices and, namely, on their planning & design. The analysis is of a merely qualitative nature and hinges on the direct experience of the Authors, acting as remediation specialists and technical and scientific consultants. Therefore, the analysis solely reflects their personal opinions.

Table 1 gives a qualitative overview of the technologies used in Italy for rehabilitating contaminated sites. The Table shows that most of the technological options available in the state of the art have been used. Largely dominant among them were ex-situ technologies, especially excavation and disposal for soil and Pump & Treat (P&T) for water. These approaches, whose use was at times inevitable, were not particularly effective in terms of environmental sustainability. Indeed, in both cases, the contaminated resource is not restored to its original or potential uses. Even if encouraging progress has recently been made, the use of in-situ technologies has remained marginal and should thus be intensified. Among the latter technologies, mention is to be made of those largely used in other countries, such as permeable reactive barriers, aerobic and anaerobic bioremediation and in-situ chemical oxidation.

EMERGENCY REMEDIATION OF GROUNDWATER

Ministerial Decree 471/99 provided that, where preliminary investigations indicated that admissible limit values (as shown in the two tables of Annex 1) were exceeded, a procedure of site characterisation and subsequent remediation was mandatory. In most cases, emergency containment measures were adopted even on a preliminary basis, especially when contamination affected groundwater.

Indeed, Ministerial Decree 471/99 defines emergency containment as "any measure that is necessary and urgent to remove contaminating sources, contain the propagation of pollutants and prevent contact with the polluting sources at the site, pending environmental remediation or permanent safety containment measures".

As is obvious, contaminated groundwater in motion may, by definition, extend the contamination, as it may reach other sensitive targets (e.g. wells for agricultural or drinking uses, surface water bodies). Nevertheless, under certain circumstances (especially in case of "older" contamination), the contamination plume may be stationary or even may shrink, e.g. by natural attenuation if the original contamination sources have been removed. Based on the experience of these years, when contamination was identified, knowledge of the local hydrogeology was not sufficient to infer an actual risk of contamination enlargement. As a result, public authorities dominantly interpreted the applicable legislation by relying on the precautionary principle and requiring the putting in place of groundwater containment systems.

Use was mostly made of hydraulic barriers (containment via extraction wells and treatment of extracted water) or physical barriers (containment via impermeable diaphragm walls with drains and treatment of drained water), usually located downstream of the contaminated site, so as to intercept the entire contamination plume.

In the case of physical barriers, lateral ones were the most common. These barriers consisted of: i) sheet piles, with or without polyurethane joints, which prevented releases along discontinuities; and ii) plastic diaphragm walls in bentonite-cement mixture, with or without geomembrane inserts. In many cases, physical barriers were preferred to hydraulic ones for two reasons: i) concerns about proper management of hydraulic barriers; and ii) public authorities' difficulties in monitoring their efficiency and effectiveness.

EX-SITU			
Technology	**Status**	**Technology**	**Status**
Excavation and disposal/treatment	XXX	Landfarming	XXX
Incineration	XX	Phytoremediation	XX
Soil washing	XX	Immobilisation	X
Biopiles	XXX	Thermal desorption	XX
Composting	XX	Pump & treat	XXX
IN-SITU			
Technology	**Status**	**Technology EX-SITU**	**Status**
Physical barriers	XXX	Vapour injection	XX
Soil vapour extraction	XXX	Bioremediation	XX
Bioventing	XXX	Reductive dehalogenation	X
Air sparging	XXX	Hydraulic fracturing	X
Biosparging	XXX	Phytopurification	XX
In-well (GCW) stripping	XX	Solidification/stabilisation	X
Multi-Phase Extraction	XXX	Permeable reactive barriers	XX
Land-farming	XXX	Electromigration	X
Soil flushing	XX	Heat treatment	X
Chemical oxidation	XX	Natural attenuation monitoring	XX

Tab. 1 - Status of application of the various technologies for remediation of contaminated sites in Italy (XXX, common; XX some full-field applications; X demonstration or pilot scheme)

Generally, emergency measures based on groundwater barriers proved to be appropriate, especially when boundary conditions permitted their fast construction and operation. This was possible when hydrogeological conditions were relatively simple and known, plume size and groundwater discharge were small and adequate or improvable local treatment systems were in place. Under less favourable circumstances, the construction of barrier systems called for major technical, economic and time-consuming efforts, which partially nullified the "emergency" character of the project (i.e. fast construction and operation), especially in the case of physical barriers.

The design of hydraulic barriers of considerable size (with high volumes of water to be extracted and a large contamination front to be contained) also provided remediation specialists with the opportunity to upgrade their skills. Reliance was indeed made on largely widespread numerical flow models, such as MODFLOW (in the most updated versions with pre- and post-processor), as well as on models used on a more limited scale, such as FEFLOW.

Nonetheless, once a barrier system (generally consisting of wells and rarely of trenches) is in place, the underlying design assumptions must be validated via piezometric and hydrochemical monitoring. These actions, whose purpose is to demonstrate the hydraulic efficiency and hydrochemical effectiveness of the system, may also offer the opportunity to fine-tune the models and simulate all normal and abnormal operating conditions of the hydraulic barrier.

Further enhancements based on horizontal wells (Porto Marghera) were proposed for sites whose below-surface structures might hinder safety and remediation efforts.

A specific problem may arise from active sources of secondary contamination, which slowly release liquid-phase contaminants. This is the case of contaminants that are poorly soluble and/or strongly adsorbed onto the solid phase (e.g. heavy metals and hydrocarbons) or of separate-phase contaminants (e.g. chlorinated solvents whose dense separate phase is dispersed in the aquifer, DNAPLs). In these instances, the volumes of water to be treated may be very high, because the process is controlled by the slow dissolution kinetics of the source, while the volumes of contaminant are typically small. It follows that treatments should extend over long periods of time until exhaustion of the source and of the plume (typically at least 5-10 years but also longer) with high operational costs (in terms of energy and reagents).

It should be stressed that the above-mentioned emergency measures were implemented prior to and had an impact on permanent remediation activities, even if they had not benefited from the in-depth knowledge arising from subsequent (preliminary & final) project planning stages.

Planning of emergency remediation

When the need for implementing emergency remedies was assessed, knowledge of the hydrogeological setting was often poor, making it difficult to plan and design barrier systems within a short time. In the case of hydraulic barriers, key issues were:
- computation of actual groundwater flow to be extracted, in a dynamic setting which should take into account: vertical stratification of the contamination; interactions with underlying aquifers; concurrent abstraction of water for industrial uses;
- possible interaction with salt water (in sites close to the sea);
- on-site availability of adequate treatment plants.

In the case of physical barriers, the planning & design process required more detailed information on the characteristics of the subsoil (primary and secondary permeability) and, above all, on strength of the bedrock into which the barrier systems were planned to be keyed. Additional factors of a potentially critical nature included the need for reaching considerable depth (several tens of metres from ground level), removing water upstream of the system and, consequently, treating contaminated water.

A problem common to both types of systems was the lack of clear criteria for assessing their effectiveness. Each emergency remediation project was inevitably associated with a piezometric and/or hydrochemical monitoring plan (often demanding and costly). However, the benefits from the project were seldom assessed prior to its implementation owing to - *inter alia* - poor understanding of the local hydrogeological setting and, at times, excessive expectations of public authorities or stakeholders in terms of short-term interpretation of the hydrochemical data collected downstream of hydraulic barriers. This situation entailed "cascade" projects (e.g. physical barriers applied after hydraulic barriers) with disputes between public authorities and private citizens.

With regard to the regulatory-legislative framework, the approval of a remediation project - as is known - replaces all the authorisations needed for its constituent activities. Nevertheless, neither Ministerial Decree 471/99 nor Decree 152/2006 require public authorities to assess or formally approve the emergency containment measures. This approach is justified under emergency conditions, as it enables remediation specialists to take prompt action without awaiting the long time needed for public approval. However, even if the emergency project does not need per se an approval, it should obtain all other authorisations needed for routine management of water releases and waste. For instance, in industrial sites, it was often difficult to treat the water extracted from the physical or hydraulic barriers placed in the water treatment systems of the local plant. Indeed, as the extracted water is regarded as waste, the industrial plant requires a specific permit. These circumstances nullified the law-makers' intent to speed up emergency response actions.

Thanks to experience, the weight to be assigned to emergency measures will hopefully be better assessed, taking into account - above all - the need for implementing fast, flexible and reversible projects. In this regard, the new text of Decree 152/2006 appears to better delimit the scope of emergency remediation measures. However, the Authors feel that the text should be improved by more accurately defining the scope, criteria and modalities of implementation, monitoring and control of emergency containment mesures.

At the same time, with regard to hydraulic barriers, characterisation plans should encompass detailed reconstruction of the hydrogeological setting of the contaminated site and of the configuration of the contamination plume, considering also the vertical stratification of the contamination. If a hydraulic barrier system proves to be actually necessary, it should be designed in such a way as to minimise the water to be extracted and make a trade-off between containment of the contamination and quantitative conservation of the resource (as part of a water resource conservation plan, where available).

Finally, a solution should be sought for the problem of authorising emergency remediation measures and/or related works. The possible options are:

1) providing that emergency mesures should be limited to cases where no authorisation is required or the owner already holds an authorisation;
2) planning a specific or alternative procedure for emergency mesures by issuing general or specific provisions.

Treatment and fate of extracted water

Contaminated groundwater from physical or hydraulic barriers requires adequate purification processes, also depending on the fate of the extracted water.

The key critical aspects are:
- use and fate of the extracted water;
- related limits to discharge and authorisation procedure;
- treatment processes to be adopted accordingly.

In principle, the ideal fate of extracted and treated (and thus "remediated") water should be the return to its original underground water body. This solution quantitatively conserves the resource and restores it to its potential uses. This solution has been rarely applied (e.g. when it enabled, among others, to counter the ingression of marine water), although it is explicitly mentioned in the legislation on remediation (Annex 3, Ministerial Decree 471/99 "*….withdrawal of groundwater for the purpose of carrying out a treatment of decontamination, including or not including reinjection into the aquifer*".

A first problematic aspect was the intersection of the legislation on remediation with the one on the control of discharges, which prohibits discharges into the subsoil. An exception is represented by Art. 11 of Directive 2000/60/EC stating that member countries "*may also authorise, specifying the conditions for: ... discharges of small quantities of substances for scientific purposes for characterisation, protection or remediation of water bodies limited to the amount strictly necessary for the purposes*". These considerations are at least in part superseded by Decree 152/2006, specifying (Art. 243, para. 2) that, by derogation from the ban on discharges into the subsoil, extracted and treated water may be reinjected into the subsoil. As indicated in the previous paragraph, the issue was compounded by judge-made law, which considers the extracted contaminated water as waste. This interpretation of the legislation made it necessary to seek specific authorisations for the purification treatment, which are not easy to obtain, especially when the water contains hazardous substances.

Another critical element was the identification of limits to discharge, to be adopted in the different contexts. As is obvious, the water to be reinjected into the subsoil must undergo a process that restores it to uncontaminated conditions (limit values of Table 2, Annex 1, Ministerial Decree 471/99). However, approaches to discharges into surface water bodies have been more heterogeneous, ranging from the adoption of the above-mentioned limits (under the precautionary principle) to the definition of these discharges as industrial discharges (presently specified in Table 3, Annex 5, third section, Decree 152/2006). For the sake of conciseness, this intricate issue will not be exhaustively covered here. Various factors are indeed at play:
- quantitative and qualitative sensitivity of the recipient water body and specification or non-specification of water quality targets and specific limits in regional conservation plans;
- presence or absence of other discharges containing identical or different contaminants;
- nature of contaminants, namely whether there are hazardous, persistent toxic and/or bioaccumulatable substances;
- emergency or permanent nature of the project, with presumably different implementation and management timescales;

- presence or absence of industrial activities which may use all or part of the extracted water and thus save higher-grade water resources;
- availability of suitable technologies and systems at reasonable costs.

As a rule in general, emergency or permanent remedies should not worsen the quality of the recipient water body (even if it is different from the one to be remediated) and should help achieve the water quality targets that are established in the conservation plan. So, the choice of limits should be made on a case-by-case basis. For instance, in the case of Lago Maggiore (presence of DDT), the water to be released is required to have a zero DDT content. This requirement involved the use of the best available technologies, so much so that the maximum content of DDT in the waters coming from the treatment system is equal to 25 ng/l. Furthermore, priority should be assigned to the re-use of extracted water in industrial cycles, possibly by loosening the limits to its subsequent discharge (as successfully done in many sites of national interest).

In this framework, the current legislation (para. 1, Art. 243, Decree 152/2006) excessively simplifies the state of the art. Indeed, it goes as far as to permit even the direct discharge of the extracted water (without any prior purification), provided that it meets the limits specified for industrial waste water discharges, without explicitly referring to quality targets for the recipient water body. This is a simple but poorly precautionary solution, given the significant difference of limit concentration values existing between contaminated groundwater and waste waters. In other terms, contaminated groundwater might be withdrawn from the subsurface and directly reinjected into a surface water body without any treatment.

From a technological viewpoint, the main problem in adopting precautionary limits for releases was the need to attain high performance in the treatment of water containing different contaminants, often in relatively small concentrations. Based on experience, this aspect was effectively solved by refining the technologies for the treatment of each type of contaminants and by developing serial treatment processes, usually in dedicated systems. Table 2 displays a qualitative list of the principal technologies used for the treatment of extracted water. Lately, P&T projects have increasingly been associated with more localised ("hot spot") measures; these measures, usually relying on in-situ technologies (e.g. stripping of volatile compounds), were often combined with remedial measures in the unsaturated zone. It is worth emphasising that a volatile compound extraction well, located near the source (high concentrations), may be much more efficient (in terms of contaminant mass extracted per day) than a groundwater extraction well placed downstream and having the purpose of blocking the entire plume. Thus, in the first instance, the remediation effect prevails, whereas in the second one the hydraulic barrier effect is dominant. This approach (more modern and more sustainable and so to be encouraged) is usually adopted to shorten the timescales of P&T projects.

Technology	Status	Technology EX-SITU	Status
Activated carbon	XXX	Ion exchange	XX
Stripping	XXX	Clariflocculation	XXX
Precipitation	XXX	Filtration	XXX
Chemical oxidation/reduction	XXX	Ultrafiltration	XX
Catalytic oxidation	XX	Reverse osmosis	XX
Advanced oxidation processes	X	Biological treatment	XXX

Tab. 2 - Status of application of different purification technologies in P&T projects in Italy (XXX, common; XX some full-field applications; X demonstration or pilot scale)

An alternative approach

As suggested above, emergency remediation of contaminated groundwater via hydraulic or physical barriers should be confined to really urgent cases (e.g. enlargement of the contamination plume, sensitive receptors, health & safety risks).

Moreover, even if the P&T approach may be regarded as well-established and reliable, preference should be given, wherever feasible, to in-situ technologies. These technologies should:
- permit emergency remediation and possible remediation without extracting groundwater, thereby conserving the potential underground resource and simplifying authorisation processes;
- use passive hydraulic processes, i.e. exploit the natural flow of the aquifer, thus minimising energy consumption;
- be based on long-term processes, tailored to the slow kinetics of the natural processes of contaminant release;
- mostly rely on subsurface systems, so as to permit the use of the property and favour the linking between emergency remedies, permanent remedies and enhancement of the economic value of the sites involved.

In this framework, reference has already been made to technologies of desorption of volatile compounds, often accompanying (rather than entirely replacing) P&T measures (see previous paragraph). Over and above these technologies, the technology of Permeable Reactive Barriers (PRBs) appears to be particularly promising, although it has not yet been applied on an extensive scale in Italy.

In the US (having the largest number of in-service PRBs) and in some European countries, the PRB technology is the focus of major research projects (basic research, pilot and demonstration schemes, e.g. the SAFIRA project in Germany) and is being rapidly applied to clean-up of contaminated groundwater (over one hundred installations in the world). PRBs proved to be particularly effective in removing chlorinated solvents (the most widespread contaminants in Italy too), by using zero-valent iron as a reactive filler for the PRB. In effect, the reaction between zero-valent iron and chlorinated solvents has been thoroughly studied and does not pose particular problems in terms of by-products. Anyway, there exist other applications with other reactive materials and for other contaminants.

As already noted, the Italian cases of application of and/or research on PRBs are rather few (to the best of our knowledge, a single full-scale application), despite the fact that PRBs are suitable for both emergency and long-term remedies (follow-up of hydraulic belt systems used for emergency response).

In its simplest and most common configuration (Figure 1), a PRB consists of a trench (thickness 0.5-1 m, depth down to 15-20 m, width even some hundreds of metres), which is dug inside a contaminated aquifer and, where feasible, resting on an impermeable lower layer.

The trench is filled with reactive material. The filler is more permeable than the aquifer material, so that the natural flow from the aquifer ensures the passage of water. The reaction between the reactive filler and contaminants rehabilitates groundwater, restoring its natural flow.

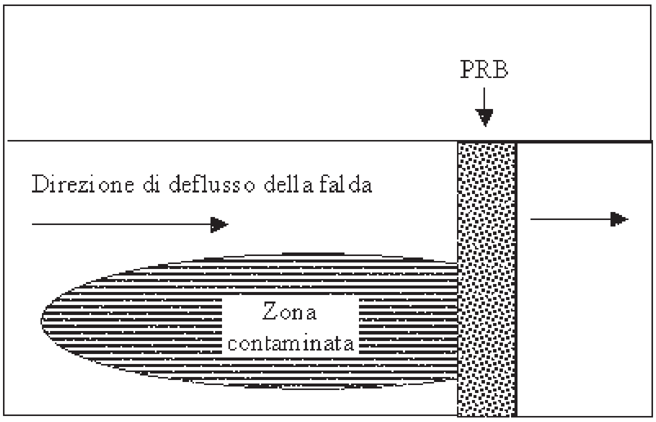

Fig. 1 - Typical configuration of a PRB
Captions: PRB, groundwater flowpath, contaminated zone

The PRB is designed to operate for many years with little or no maintenance. All or most of its components are placed underground. Piezometres upstream and downstream of the PRB monitor its hydraulic and chemical efficiency.

In some instances, instead of a continuous trench, resort is made to an impermeable trench, which conveys water towards a less wide reactive zone (tunnel-and-gate configuration). This configuration could be suited for retrofitting emergency remediation systems initially based on impermeable diaphragm walls, thereby making it unnecessary to treat the drained water in an above-ground purification system.

REMEDIATION OF SOIL AND GROUNDWATER

With regard to soil remediation, the prevailing approach was based on excavation of contaminated soil and subsequent disposal (Table 1). To minimise the volumes to be disposed of, use was often made of (mechanical or hydraulic) screening; in this way, the most-coarse grained fractions of contaminated soil were recovered and reused on- or off-site. The most frequently used on-site recovery technologies include biological treatments (usually biopiles and landfarming, less frequently phytoremediation) or physico-chemical treatments (soil washing). Conversely, the use of heat treatments (thermal desorption at low and high temperature) encountered difficulties that are typical of the Italian context (e.g. waste incineration).

As previously stated, groundwater remediation projects have often been conditioned by prior emergency response remedies, leading to prevalence of the P&T approach. Interestingly, this situation focused the attention on two critical aspects: effectiveness of the barrier system and treatment and fate of the extracted water. A third aspect, often neglected but of crucial importance when passing from emergency measures to long-term remediation, is represented by the effects of the emergency measures on groundwater remediation. As is obvious, a P&T system used for emergency response is the natural candidate for and remains in place also for subsequent remediation projects. However, in the latter instance, its role should change, because the flow of clean water from upstream is key to groundwater regeneration. Hence, in the case of a hydraulic barrier, the remediation project should involve an optimisation of the extraction system so as to renew the groundwater or, at least, a computation of the time elapsing from the installation of the barrier system to actual renewal of the groundwater.

In-situ technologies are slowly and growingly been used for both soil and groundwater. At least in terms of projects, there are examples of in-situ chemical oxidation (ISCO), geoelectrochemical and bioremediation systems, operating under both aerobic (slow oxygen release compounds) and anaerobic conditions (reductive dechlorination of chlorinated solvents). Until now, the chief obstacle to the development of these techniques has been the assumption that, by their use, the low concentration limits considered as acceptable by Ministerial Decree 471/99 cannot be met. Failing literature reports about their application down to that limits, this assumption has prevented them from being field- or pilot-tested and, thus, further developed in Italy (see next paragraph).

Planning of a remediation project

It goes without saying that planning a remediation project is a sensitive and complex process. Ministerial Decree 471/99 divided this process in two stages: preliminary and final.

Preliminary project planning was the central stage of the process, as it was expected to: i) define the general scenario of the project (remediation, remediation with risk-based remedial measures, permanent containment) and its goals; and ii) select the technologies to be used on the basis of the conceptual model of the site, of the initial screening of available technologies and, possibly, of a risk analysis. Under this approach, preliminary project planning also involved all the tests required for determining whether the selected technologies were applicable to the case under review, including pilot and field tests.

This approach correctly reflects the requirement that the scenarios of and technical options for a remediation project be checked on a case-by-case basis, considering: i) the complex interactions existing between contaminants and contaminated media; ii) environmental conditions, which have a major site-specific impact on the efficiency of the selected technologies; and iii) need for implementing the project at full field and over long periods of time. All these aspects call for good planning of the project.

Based on the experience of the Authors, this approach was rarely put into practice, as the responsible parties were generally reluctant to bear the burden of the often long and costly experimental tests. This was particularly true of the preliminary project planning stage, i.e. failing prior endorsement of the basic scenario and technological choices by the relevant public authorities. Nevertheless, even final project planning was poor and rarely based on site-specific experimental results.

These weaknesses appeared even when the selected technological approaches were very straightforward. For instance, the (dominant) excavation and disposal approach was often associated with sieving and in-situ reuse of the uncontaminated and more coarse-grained fraction of the soil (with or without prior washing). Obviously, this approach minimises the volume of contaminated material to be disposed of, but it must be based on two simple, reliable and relatively cheap tests: efficiency of industrial-scale sieving in relation to mesh size and actual absence of contamination in the sieved fractions. Failing these tests (i.e. by resorting to laboratory-determined grain sizes for the entire project), project estimations may be grossly wrong and it will not be easy to correct them on the jobsite, also taking into account that waste management is strongly regulated.

Poor project planning had more repercussions on in-situ technologies, which are highly dependent on the characteristics of the site and which rely on less standardised planning procedures. The problem was compounded by public authorities' and control agencies' mistrust towards this approach, owing to complexity of project planning and of the related control activity (see, again, Article 11 of the above-mentioned Directive 2000/60), as well as to concerns about the formation of in-situ by-products (secondary contamination).

For instance, another in-situ technique whose application has been limited so far in Italy is in situ chemical oxidation (ISCO), which consists in injecting a chemical oxidant directly into the soil or groundwater. The goal of the treatment may be total degradation or merely conversion of the contaminant to oxidised products, which may be subsequently biologically degraded. The performance of the process is highly conditional upon the characteristics of the soil. Fig. 2 shows a typical in-situ oxidation process for groundwater.

Chemical oxidation may also be conducted by soil flushing, i.e. injecting an extracting agent (e.g. a surfactant) into the saturated zone; the agent may alter the properties of the interface between the soil and the contaminant, favouring its dissolution. The mixture of injected fluid and extracted contaminants is captured by the extraction well, from which it is fed to an ex-situ oxidation treatment system. Soil flushing avoids the production of oxidation compounds directly in the aquifer and, consequently, their possible uncontrolled diffusion. However, what cannot be avoided is the generally high content of soil substances in the water to be treated; these substances

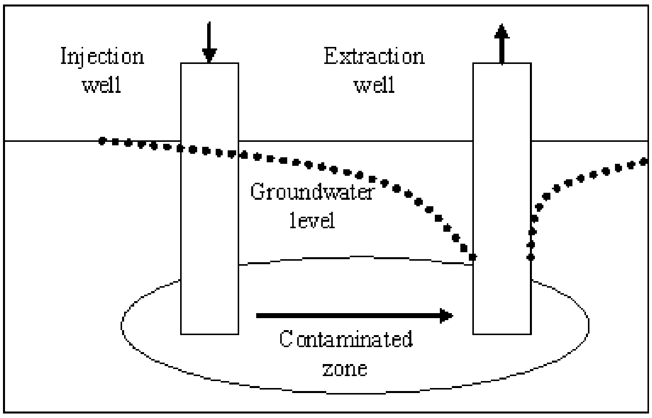

Fig. 2 Typical in-situ oxidation process

may make the treatment and disposal of the treated effluent difficult. Additionally, if the extracting agent is expected to be reused (in order to reduce costs and avoid an excessive use of oxidation reagents), it should be separated from the solution prior to treatment.

Contaminants which may require an ISCO treatment include volatile and semi-volatile organic compounds (organochlorinated and IPA compounds, PCBs and pesticides) and also heavy metals. In particular, oxidation of heavy metals reduces their mobility in aquifers, by precipitating their oxidated forms. However, it should be checked whether the water contains redox-sensitive elements, which may be oxidised to more soluble forms (Cr, V, Se, Pb and Mo).

The short description given above suggests that the in-situ use of this techniques demands a deep understanding of the interactions of the oxidising reagent not only with contaminants but also with the other compounds contained in the water and in the soil, so as to avert the formation of undesirable by-products.

On the latter aspect, a first step forward was the drafting of a protocol by "Agenzia per la Protezione dell'Ambiente" (national environmental protection agency) and "Istituto Superiore di Sanità" (national health institute). The protocol sets out the general criteria for testing and planning of in-situ projects based on the addition of chemical compounds and to be carried out under well-controlled conditions.

For the time being, the protocol only describes laboratory tests for chemical oxidation and generally requires the identification of by-products, if any. In the future, this requirement might be met by adopting ecotoxicity criteria and tests. These tests may rapidly determine the overall effect of potential by-products at an early stage and, where necessary, be followed by more in-depth and specific analyses. In the future, protocols of this type should be extended to pilot-scale field feasibility tests, which may better model actual conditions and performance (see also next paragraph).

With regard to the new legislative framework (Decree 152/06), which hinges upon a single level of project planning (final project of remediation or other measures), the Authors feel that it will tend to worsen the general difficulty of carefully planning the project on the basis of site-specific experimental tests. A double level of project planning should in fact be maintained. The preliminary planning activity should not only screen and select scenarios, goals and technologies, but also formulate a detailed experimental protocol, to be applied as part of the final project for the selected technology. Formal approval of the preliminary project would also replace all the authorisations needed for and representing an additional hindrance to conducting field and pilot tests.

Another option, especially for particularly complex cases covering large areas, is to develop a preliminary project where the remediation activity is split into successive modules and the testing activity is full-scale conducted as part of the first module. A similar approach (albeit at final project planning level) was adopted for Porto Marghera, a site of national interest. In this case, under a detailed technical and procedural operational protocol, the performance of the candidate technologies will be tested directly in the initial full-scale modules. This approach has made it possible to: i) more rapidly plan the remediation project, relying on advanced and innovative in-situ techniques (e.g. chemical oxidation, geoelectrochemical treatment and anaerobic bioremediation); and ii) gradually optimise the use of these technologies until reaching their limits; however, these limits should lie below pre-determined minimum target values, to be validated via risk analysis.

Operational protocols for assessment and planning

The previous paragraph has highlighted that operational protocols are critical to good planning. Based on existing data and on parameters collected through field surveys, these protocols can guide the assessment of the best available technology, optimise the quality and quantity of the data to be gathered and minimise the costs and timescales for project selection and planning. In practice, a protocol of this type translates into a characterisation procedure, whereby project assumptions are tested via specific measurements and tests, taking into account the types of contaminants considered, the remediation technology/ies to be assessed and the characteristics of the investigated site. Therefore, such a protocol is intrinsically much more specific than a general characterisation procedure which merely determines the extent and type of contamination (such as the one referred to in Decree 152/2006 as the first stage of assessment of the need for a remediation project), even if part of the necessary data may overlap those that a detailed and site-specific risk analysis requires.

By way of exemplification, reference will be made hereafter to in-situ bioremediation of aliphatic chlorinated solvents, a borderline case in terms of complexity. At international level, two protocols deal with the assessment of natural attenuation or accelerated bioremediation. The first, issued by the US EPA ("Technical protocol for evaluating natural attenuation of chlorinated solvents in groundwater", Weidemeier et al., 1998) is intended to establish whether, in the investigated aquifer, natural attenuation processes (i.e. the sum of immobilisation, adsorption, dilution and biological degradation processes) are capable, by themselves, to rehabilitate the site within a reasonable timeframe and under safe environmental conditions. The second is the so-called RABITT technical protocol ("A treatability test for evaluating the potential applicability of the reductive anaerobic biological in situ treatment technology to remediate chloroethenes"), arising from co-operation work between the Battelle Memorial Institute (Columbus, Ohio), the Cornell University (Ithaca, New York), EPA (Ada, Oklahoma) and the US Air Force Armstrong Laboratory (Tyndall AFB, Florida). This protocol takes a more comprehensive approach which includes not only the monitoring of natural attenuation, but also a treatability test having the purpose of determining the potential acceleration of in-situ reductive dechlorination via specific cations, such as addition of reducing substrates.

Both protocols (at least in the initial stage) are based on scores that are assigned to the various characteristics of the investigated site. The sum of the scores ranks the sites according to their potential of fulfilling the decontamination assumption underlying the protocol. Based on this ranking, the decontamination modality may be accepted, discarded or verified via more detailed characterisation. Hence, the protocol guides users through a decision-making process where the data are organised and used to determine whether the candidate technology deserves further consideration. The protocol is interrupted when it indicates that site characteristics or other considerations (legislation or local specificities) prevent the candidate technology from being used or make it uncompetitive with other ones.

More recently, based on the above protocols, an Italian operational protocol on in-situ bioremediation of groundwater contaminated by chlorinated solvents was drafted. The protocol results from the Italian research project on "Bioremediation of groundwater contaminated by chlorinated solvents: study of advanced in-situ and ex-situ processes and preparation of a protocol for assessing strategic options for remediation". The project was jointly implemented by the Departments of Chemistry, Hydraulics, Transportation and Roads of the University of Rome "La Sapienza", "Istituto di Ricerca sulle Acque" (IRSA, water research institute) of "Consiglio Nazionale delle Ricerche" (CNR, national research council) and the Province of Milan.

For details, the draft protocol is included in the Proceedings of the Conference "La bonifica dei siti contaminati: normative e tecnologie a confronto", Convegno Internazionale e Progetto Trans-IT, 23/24 Novembre 2006, Provincia di Milano (see footnote 2). The following is an outline of the document.

The protocol consists of 4 main stages, which may be further divided into multiple sequential or parallel activities (Figure 3).

Stage 1: Preliminary site assessment

The first stage is an extensive reconnaissance of the characteristics of the site. This stage ends with a preliminary classification of the site according to the applicability of in-situ bioremediation, based on anaerobic reductive dechlorination (RD, i.e. a serial reduction process removing chlorine atoms from the organic skeleton of the molecule, e.g. from tetrachloroethylene to ethylene. Reliance is made on histor-

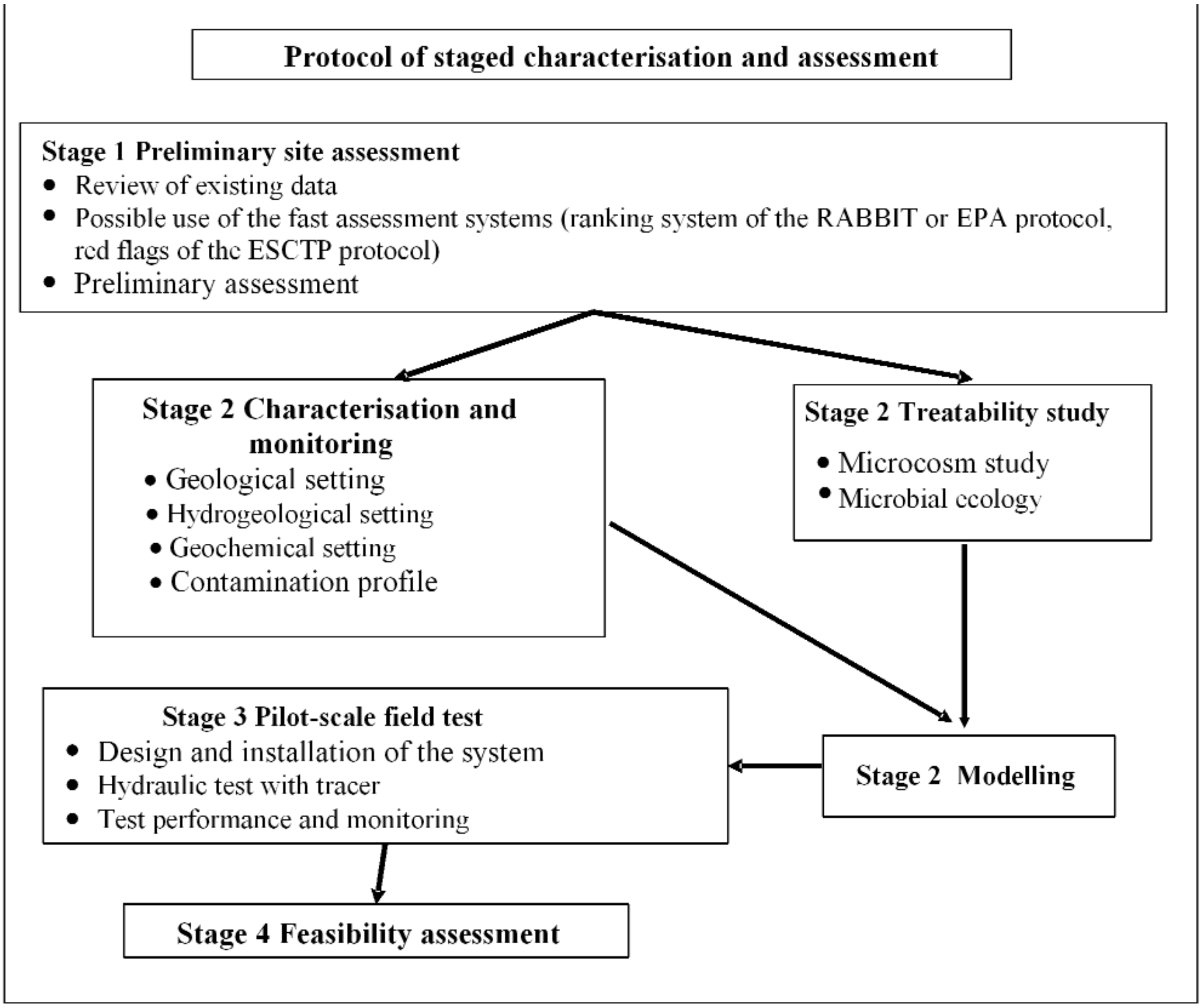

Fig. 3 - Conceptual diagram of the protocol

ical, local, chemical, geochemical and hydrogeochemical data. Most of these data usually derive from the preliminary characterisation stage, which precedes the application of the protocol and which only needs to be reorganised and tailored to the requirements of RD.

Assessment of the contamination includes all the parameters defining its type and extent. Among the characteristics of particular interest for RD, mention is to be made of the presence, concentration and distribution of low-chlorinated products (e.g. dichloroethylene DCE and vynilchloride VC), which give a measure of the natural RD potential. Likewise, the occurrence of co-contaminants (hydrocarbons, aromatic solvents, metals) may positively or negatively affect RD. For example, high concentrations of heavy metals may inhibit microbial activity, whereas some organic contaminants may act as electron donors and ease RD, also by consuming electron acceptors which may compete with RD. This analysis is also aimed at gaining insight into the spatial distribution of contamination and, namely, at determining whether it suggests a non-aqueous dense phase (DNAPLs) which may impact on the strategy of addition of external substrates.

The geochemical setting practically describes the existence or probability of obtaining environmental conditions suitable for RD. In addition to general characteristics, such as pH, alkalinity and temperature, the geochemical study assesses the parameters affecting the redox conditions of the system, as RD requires highly reducing conditions. Therefore, the following parameters are evaluated: current redox conditions (redox potential), presence of electron acceptors (oxygen, nitrate, sulphate), of electron donors (dissolved organic carbon) and, finally, of products of typically anaerobic metabolism (methane, hydrogen sulphide). Other compounds of mineral origin that may also affect redox conditions (iron and manganese compounds) are also investigated, where necessary. Naturally, the geological setting plays a role of paramount importance, since the protocol assesses the potential of accelerating RD by the addition of substrates.

The hydrogeological setting is mainly defined by hydraulic conductivity K (m/s), which is considered to be fairly indicative of the set of hydrogeological properties of the site.

Stage 2: Characterisation and treatability study

This stage consists of three interconnected activities which may in part be conducted in parallel.

Stage 2a) - Characterisation

Site characterisation is first completed on the basis of the findings from the preliminary stage. Additional characterisation involves field work and ad-hoc measurements of the distribution of contaminants and of the hydrogeological and geochemical characteristics of the site (already investigated in the first stage), with a view to corroborating the applicability of the protocol and planning subsequent stages. Thus, the type and quantity of investigations to be made should result from a trade-off between technical and economic requirements. The methodological approach to be taken to the planning of investigations should have a hierarchical structure and identify priorities; the latter will be followed by in-depth analysis of specific areas requiring more detailed data. Indeed, gaps in the characterisation stage may result into a non-homogeneous distribution of amending agents in the area where the dechlorinating microbial activity is to be stimulated.

Frequently, additional characterisation is conducted at small scale, especially when the presence of DNAPLs is likely (knowledge of their approximate location is needed). In this stage, samples of soil and groundwater, to be used for the microcosm study, are collected.

Stage 2b) - Treatability study

Microcosm studies are laboratory experiments which are conducted to determine the biological reactivity at the site on the contaminated groundwater. In these studies, soil and groundwater are placed in contact with each other inside serum bottles, so as to replicate the conditions that naturally occur in groundwater or that can be created by the addition of appropriate amending substances (nutrients, electron donors, etc.) to the aquifer. To a large extent, the need for conducting microcosm studies arises from the fact that contaminated aquifers (just as the majority of environmental systems) differ in terms of microbial composition and the interactions of their microbial composition with the environment (geology, hydrogeology and geochemistry) are very complex. As a result, analytical data on groundwater and subsoil composition are generally not sufficient to indicate whether a given aquifer contains microorganisms and whether its environmental conditions are conducive to bioremediation.

More specifically, microcosm studies respond to the following questions:

- Does the aquifer contain native microbial populations capable of performing RD of the chlorinated contaminants of interest?
- Can RD processes be accelerated by adding an appropriate electron donor to the aquifer?
- Does RD of chlorinated contaminants cause the formation of unchlorinated and non-toxic products, such as ethane or ethylene, or only lower-chlorinated products?
- What about the contaminant RD rates (order of magnitude)?
- How much electron donor is required to sustain RD of chlorinated contaminants, taking also into account any metabolism which may compete with RD in terms of consumption of the electron donor?
- Does groundwater contain substances that are toxic or inhibit biological activity?

The first of these questions may also be answered by the use of advanced microbiological characterisation methods. In effect, in anaerobic bioremediation of chlorinated solvents, a close correlation between dechlorinating activity and microorganisms was repeatedly reported. In particular, complete RD of chlorinated ethenes (and thus the presence of the harmless ethylene in groundwater) was positively correlated with the occurrence of microorganisms of the *Dehalococcoides* genus in groundwater. Techniques identifying/quantifying *Dehalococcoides* and/or other microorganisms that are significant for in-situ remediation (e.g. microorganisms fermenting the electron donor and producing the H2 required by Dehalococcoides) may improve the monitoring & control of the biodegradation process.

Findings from microcosm studies should be evaluated and interpreted in view of adequately choosing field test conditions.

In particular:

- any condition and/or electron donor promoting complete dechlorination of the chlorinated contaminants to ethylene or ethane or producing a substantial amount of these compounds may be regarded as particularly favourable;
- actual field applicability of the selected electron donor (e.g. soluble vs. insoluble) should be assessed, taking into account the systems available for injecting it into the aquifer and the hydrogeological profile of the site;
- for the selected electron donor, the amount necessary to completely dechlorinate a given amount of chlorinated solvents should be determined (considering also the use of the electron donor by competing metabolisms, such as nitrate and sulphate reduction, methanogenesis, acetogenesis, etc.);
- based on the results of microcosm studies, the RD rate should be estimated. This estimation may be used in the planning of the duration of field tests and full scale remediation. If no microcosm has evidenced the formation of final unchlorinated products, additional microcosm studies should be conducted; in these studies, exogenous microorganisms (e.g. *Dehalococcoides* spp.) capable of degrading the investigated contaminants (based on literature data) should be added to the groundwater. If these studies yield positive results (complete dechlorination to ethane or ethylene), the possibility of inoculat-

ing the aquifer with an appropriate amount of these microorganisms during field tests may be explored.
- If, as a result of the treatments made, the groundwater shows high concentrations of intermediate products of dechlorination (e.g. cis-DCEs or VCs), of fermentation (e.g. acetate, propionate), Fe (III) or Mn(II), then the possibility of conducting an aerobic treatment of the water, after the anaerobic one, in order to bring the concentration of these substances below the regulatory limits, should be explored.

Stage 2c) - Modelling

Based on data already available or collected upon site characterisation, a model may be built; the model will simulate the physical reality of the hydrodynamic and dispersive behaviour of the aquifer.

The modelling analysis is a sequence of interconnected stages, which should give an adequate feedback so as to give rise to an iterative process. The process should comprise:
- definition of goals and related choice of the types of model to be built;
- development of a preliminary conceptual model of the site on the basis of ad hoc collected and already available data;
- analysis of and more in-depth understanding of the assumed model, so as to establish whether it lacks any specific data and assess the feasibility of a possible more detailed characterisation stage;
- analysis of the sensitivity of the model to the change of its parameters, so as to estimate the level of uncertainty of the simulations.

At the end of Stage 2, a new feasibility assessment should be conducted, by combining all the data deriving from additional characterisation and the treatability study and also relying on modelling. Based on the collected data, the following elements should be determined:
- type of remedial action to be implemented and/or which is practicable (partial reduction of the source, remediation of the plume, containment of the plume);
- modes of implementation of the remedial action (type and quantity of amending substance, modes of addition);
- characteristics and modes of performance of field tests, so as to validate pilot-scale results.

Stage 3: Field testing

Planning and implementation of field tests are the last stage of the methodological approach exploring the possibility of full-scale implementing a bioremediation project based on anaerobic RD. The key goals of field tests are:
- detailed verification of the fluid dynamics of the system at local scale, usually with tracers;
- fine-tuning and optimization of systems for administering the amending substances;
- verification of the experimental results obtained from microcosm studies, under conditions that are closer to reality;
- collection of data for designing full scale treatment at the investigated site.

Preparation of the test (siting and tentative preliminary project) should be initiated as soon as characterisation results indicate conditions favouring the process, or in parallel with detailed laboratory tests (microcosm tests). This aspect takes on particular importance, considering that red tape in the test authorisation procedure may unexpectedly lengthen the project timescales, deferring the installation and testing of the system. Furthermore, it should be immediately checked whether local authorities' policies may limit the choice of the planner or designer (e.g. whether reinjection of the amended groundwater into the subsoil will be allowed or not.

Finally, the protocol gives an example of design of a recirculation test. The principle underlying the test is to develop a system capable of distributing the amending agents (selected on the basis of the microcosm test) in the contaminated aquifers under controlled hydraulic conditions. From this standpoint, the system should be designed so as to:
- create a hydraulically controlled reactive volume in the aquifer;
- monitoring and, possibly, varying its time of residence inside the reactive zone;
- adequately mixing the added amending agents with the groundwater.

Based on the overall results from the testing activity, the following stages may be started, i.e. detailed design of the remedial action.

TOWARDS A SUSTAINABLE APPROACH TO REMEDIATION OF CONTAMINATED SITES

The experience accumulated in these years of application of Ministerial Decree 471/99 infers that advanced, cost-effective and environmentally sustainable technologies can and must be developed and correctly implemented in Italy.

The review of the state of the art suggests that development and implementation efforts should be focused on sustainable technologies that:
- conserve the potential uses of the environmental resource, qualitatively and quantitatively;
- minimise waste generation and groundwater extraction;
- are fully consistent with the activities carried out in the affected areas and with the related development programmes.

To achieve these targets:

a) the approach should pass from the presently dominant excavation/removal for soil and P&T for water (waste- and energy-intensive) to development and implementation of in-situ technologies (knowledge-intensive), i.e. to an approach that is supported by: i) careful and targeted characterisation of the site involved; ii) thorough knowledge of the phenomena that occur naturally, as well as those that are induced by the interaction between technologies and environmental boundary conditions; iii) good planning and management of the technologies. Among in-situ technologies, priority should be given to those that are sufficiently "mature" (at least 50-100 cases of application at international level), although more adequate implementation and integration of procedures at national level are required. This is the case of (aerobic and anaerobic) bioremediation, electrochemical technologies, chemical oxidation and permeable reactive barriers.

b) the approach should be source-oriented; in other terms, it should rely on space-concentrated actions, with a view to singling out and removing or mitigating secondary sources (adsorbed contaminants, separate-phase contaminants); also in this instance, the projects imply a thorough knowledge of site-specific conditions. Slow release of contaminants should be taken into account when planning costly investments in remedial projects that extend over many years (e.g. P&T). Attention should be paid to cases of complex contamination arising from multiple types of contaminants (multi-purpose technologies, "trains" of technologies).

c) for developing in-situ technologies, the need arises for developing advanced methods of site characterisation (upstream of the remediation process), including combination of different techniques (chemical, geophysical, microbiological and molecular biology), identification of secondary sources (LNAPLs and DNAPLs, reconstruction of vertical profiles, assessment based on mass and not on concentration) and leading-edge modelling.

d) Finally, methods for evaluating and mitigating possible secondary impacts (downstream of the process) should be further developed: assessment of changes induced by the application of technologies to environmental matrices (texture, organic component of soils, biological activity) and of potential toxicological and ecotoxicologial impacts (development and validation of integral assessment tests), monitoring (e.g. migration of biological components), development of intrinsically safe technologies (high sensitivity to contaminants).

More generally, greater commitment to and co-ordination of public and private research can and must yield all the knowledge and procedures that are needed to further develop advanced technologies, thereby proceeding towards a sustainable approach to remediation of contaminated sits.

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2) "Biorisanamento anaerobico in situ di falde contaminate da solventi clorurati. Proposta di protocollo di indagine per la valutazione di fattibilità" by M. Majone, M. Petrangeli Papini, F. Aulenta, P. Viotti, M. Leccese, V. Tandoi, S. Rossetti, C. Cupo. The publication was co-funded by the Ministry of the Environment and Land Protection in compliance with Programme PR.3.29 (public call for tenders of 20 October 1999, published in the Gazzetta Ufficiale, Serie Generale no. 281 of 30 November 1999) and by CNR ("Gruppo Nazionale per la Difesa dai Rischi Chimico-Industriali ed Ecologici - GNDRCIE" (national task force for protection from chemical, industrial and environmental hazards, Department of Civil Protection). The full text of the document (in italian)is included in the Proceedings of the Conference "La bonifica dei siti contaminati: normative e tecnologie a confronto", Convegno Internazionale e Progetto Trans-IT, 23/24 Novembre 2006, Provincia di Milano, (annex to the presentation on "Biological Source Treatment for remediation of chlorinated solvents: the case study of Rho site (ex-Chimica Bianchi)", by the University of Rome, UFZ and the Province of Milan).