Ringrazio la mia famiglia che mi ha sostenuto in questi anni,
il Prof. Sgarbossa per la sua disponibilità e competenza,
il Prof. Raga e lo staff di ARPAV-Mestre, Arkema, R&C e Syndial
che mi hanno dato la possibilità di sviluppare questa tesi.

Index

PART 1: BACKGROUND ELEMENTS

PART 2: MATERIALS AND METHODS

PART 3: RESULTS AND DISCUSSION

Acronyms

ARPAV	Veneto regional environmental prevention and protection agency
BCF	Bio Concentration Factor
CEC	Cation Exchange Capacity
CSC	Contamination threshold concentration
CSR	Risk threshold concentration
D.lgs.	Legislative Decree
D.M.	Ministerial Decree
DC	Direct current
ECRT	Electro Chemical Remediation Technique
ISCO	In Situ Chemical Oxidation
ISS	Italian Superior Institute of Health
MATTM	Environment, territory and sea protection ministry
MPE	Multi Phase Extraction
PAH	Polycyclic Aromatic Hydrocarbons
PRB	Permeable Reactive Barrier
PVC	Poly Vinyl Chloride
SIN	Site of National Interest
SVE	Soil Vapor Extraction
VCLA	Limit acceptable concentration values
VCM	Vinyl Chloride Monomer

Extended abstract

La contaminazione da metalli pesanti nel SIN di Porto Marghera rappresenta, ancora oggi, un problema ambientale di primaria importanza; i dati acquisiti durante la caratterizzazione pregressa del sito hanno dimostrato la presenza di Zn, Al, Fe, Hg in concentrazioni superiori di oltre 10 volte le prescrizioni di legge. La natura fortemente eterogenea del suolo superficiale e la presenza di materiale argilloso nello strato insaturo più profondo, hanno pesantemente inciso sui risultati delle precedenti campagne di bonifica nel sito.

In questo studio, circoscritto all'area VP_38 del Vecchio Petrolchimico, viene valutata la fattibilità di una bonifica elettrochimica, in grado di rimuovere i metalli nel suolo di frazione fine, grazie ai risultati forniti dalla speciazione del contaminante trovato in concentrazioni superiori ai limiti di legge, il Mercurio. La bonifica elettrochimica (ECRT) è in grado di rimuovere solamente le frazioni mobili o mobilizzabili del contaminante attraverso l'uso di soluzioni complessanti e l'imposizione di un campo elettrico. L'argomento principale della tesi non è la speciazione stessa e la sua metodologia di laboratorio ma il suo ruolo e l'importanza dei suoi risultati da un punto di vista più ingegneristico e pratico ai fini della valutazione della bonifica; più precisamente, attraverso la speciazione si è dimostrato come si possa determinare, a priori, la frazione mobile-mobilizzabile e quindi rimovibile attraverso la tecnologia di bonifica scelta.

La speciazione è stata eseguita sui campioni di terreno prelevati da un area di circa 1000 m^2 *nella quale, durante una caratterizzazione pregressa, erano state trovate concentrazioni di Mercurio totale pari a 270 mg/kg. A fronte delle concentrazioni trovate, gli obbiettivi di bonifica sono stati fissati, in termini di Mercurio totale a 13 mg/kg. Il campionamento, riguardante solamente la porzione di terreno insaturo, è stato diviso in due campagne differenti tra Luglio 2014 e Marzo 2015; in totale sono state scavate 16 trincee fino alla profondità di 1,5 m dal piano campagna. Per ogni trincea sono state prelevate due aliquote di suolo rappresentative delle frazioni 0-1m e 1-1,5m di profondità in virtù della natura estremamente variabile della composizione del suolo. Su ogni campione sono state eseguite: analisi chimiche per verificare la presenza del solo Mercurio tra i composti previsti da legge, analisi fisiche per determinare il tipo di suolo e relative caratteristiche, analisi chimiche standardizzate per determinare le concentrazioni di Mercurio totale e analisi chimiche sperimentali per la speciazione del Mercurio. La valutazione del Mercurio totale, svoltasi con metodologia standard EPA 6010C e sperimentale in due sessioni differenti, è stata eseguita tramite estrazione in acqua regia e lettura in ICP ottico. Al contrario, per la speciazione è stata utilizzata unicamente una tecnica sperimentale, in corso di validazione, che sfrutta la combinazione di termo-desorbimento, gas cromatografia e spettrografia di massa. Nel dettaglio sono state individuate le frazioni: Mercurio organico (Metil-Mercurio Cloro, Dimetil-Mercurio Cloro e Bifenil-Mercurio Cloro), Mercurio metallico, Mercurio solubile in acqua e Mercurio residuo (Calomelano e Cinabro). In*

tutti i campioni analizzati, tra tutti i composti previsti dal D.lgs. 471/99, sono state trovate concentrazioni superiori ai limiti di legge solamente del Mercurio; i risultati riguardanti la concentrazione del Mercurio totale hanno dato valori sensibilmente diversi a seconda del metodo di estrazione in acqua regia e lettura in ICP EPA 6010C o sperimentale seguiti. I risultati della speciazione, supponendo la validità del metodo, hanno dimostrato in maniera similare in tutti i campioni la preponderanza della frazione immobile (Cinabro) in percentuale dal 80% al 90% sul totale mentre la specie Calomelano raramente supera il 3% sul totale. Le concentrazioni di Mercurio metallico variano in percentuale dal 5% al 10% del Mercurio totale mentre la frazione solubile in acqua non supera lo 0.5%. Le frazioni organiche del Mercurio non hanno raggiunto i limiti di sensibilità dello strumento tranne nel caso del Bifenil-Mercurio che non supera lo 0.3%.

Noto che l'ECRT è in grado di rimuovere la parte mobile o mobilizzabile del Mercurio (nello studio rappresentate da Mercurio organico, solubile in acqua e metallico), che è stata dimostrata essere una parte minoritaria del totale, si suppone che le concentrazioni finali siano paragonabili a circa 70-80% della concentrazione iniziale in termini di Mercurio Totale. Concludendo, non solo non sembra verosimile il raggiungimento dell'obbiettivo di bonifica e la conseguente fattibilità del metodo ma, allo stesso tempo, non sembra che venga rispettato un approccio scientifico nell'identificazione degli obbiettivi della bonifica stessa. A conferma della tesi è stata prodotta un'analisi di rischio speditiva che ha confermato la sovrastima del rischio e degli obbiettivi di bonifica per quanto riguarda l'approccio con il Mercurio totale. La metodologia seguita rappresenta una novità nel settore che, fino ad ora, ha fatto riferimento unicamente al dato del Mercurio totale; inoltre, a dimostrazione del fatto che la speciazione fornisce un'informazione imprescindibile ai fini della valutazione del rischio e degli obbiettivi di bonifica, il Ministero ha recentemente introdotto, ai fini dell'analisi di rischio, le forme più comuni del Mercurio speciato all'interno del database ISS-INAIL.

Abstract

In this study a new approach for feasibility assessment of an ECRT remediation is evaluated thanks to metals speciation analysis. The need to know in advance the fractionation of the pollutant, that the ECRT remediation has to deal with, seems to be of primary importance; in particular, the quantification of mobile species and fractions that may be mobilized seems to be necessary to assess the expected efficiency of the remediation. The results, obtained by 12 speciation‘s samples extracted from the polluted site in Porto Marhera, had proved that up to the 90% of the total Mercury is present as immobile and non-risky HgS; consequently, the remediation target of 13 mg/kg of total Mercury seems not to be achievable.

Thesis activity

The thesis activity was chosen in order to get practical experience and further knowledge about remediation of contaminated sites thanks to the collaboration between the University of Padua, ARPAV public agency and Arkema private company. The internship period gave me the possibility to analyze in detail the project‘s features and the project‘s variation, to face with legislation requirements and to gain understanding of the sampling procedure and environmental data analysis; at the same time, the intercourse with Arkema offered me a complete view about a project management and the several problems that may arise during its engineering. In addition to public relationships with Syndial and Arkema, during the thesis development I worked for:

- Review about Porto Marghera characterization;
- Critical review about remediation projects approved by the ministry;
- Literature review about metal‘s remediation and ECRT application.

On the other hand, during the experimental part of the study I was involved into:

- Soil sampling campaign;
- Mercury speciation analysis.

Objectives of the study

It should be pointed out that during the thesis period the objectives of the study had substantially changed: at first, the thesis was aimed to assess the efficiency of the ECRT modules that should have been started during the study period; later on, due to a series of inconveniences the implementation of the scale up seemed to be almost impossible. As a consequence, the interest had moved to a close examination of the problems that arose during the engineering of the project in order to justify and explain that the missed goal was not a failure of the technique but the consequence of the effects of a narrow minded legislation and intrinsic proprieties of the application. More precisely, this study was developed in order to:

- Assess the feasibility of the application by the use of speciation analysis as a preliminary tool;

- Contextualize the feasibility of the application in light of strictly legislation requirements and cost analysis.

I want to underline that some features that had been used during the evaluation and discussion of the study objectives are still covered by patent and industrial secret.

Introduction

Porto Marghera is sadly notorious for the environmental consequences related to almost 40 years of wicked industrial production and lack of environmental protection care. Due to the high heterogeneity of the pollution, the huge surface occupied by the area and the high sensitivity of the Venice lagoon as the target of pollution, Porto Marghera had been listed among the Site of National Interest (SIN) since the 1998; just one year later, the need of a programmatic text (*Accordo per la chimica*) for the recovery of Porto Marghera seemed to be of primary importance not just for environmental problems but also for economic and social reasons. As a consequence, due to the high complexity of the remediation a further text (Master plan,2000) had been adopted in order to give guidelines and technical considerations about the remediation of the area. Even after such a long period, the area had been minimally recovered and restored for industrial activities; heavy pollution, strict legislation and high costs for remediation seem to affect the new rise of the site.

Characterization plans had proved that the majority of the soil of the area are a mixture of by-products of past industrial activities made up with gravels and sandy materials; however a general layout of the stratigraphy could be described by the presence of a top soil layer (mainly backfill soil composed by sandy material mixed to cobbles, gravel, clay, silt and organic materials), a top impermeable layer (composed by grey-brownish colored clays mixed with few percentages of silts), a superficial aquifer (composed by fine grained gray sands with few percentages of silts) and a secondary impermeable layer (which composition is mainly characterized by gray silts and clayey silts). On the other hand, the wide and abundant presence into both soil and groundwater of by-products, related to PVC manufacture and Cloro-soda plants had been demonstrated; at the same time other pollutants such as iron, manganese, chlorinated solvents and hydrocarbons had been found in the site. Data from the Veneto region notice that, concerning contaminated soils, almost the 54% of the total area had been characterized and planned by an approved remediation plan, whereas about 36% of the site had been not interested by remediation project so far; just the 5% of the area is being remediated. Dealing with contaminated groundwater, almost the 50% of the total area had been planned by an approved remediation plan whereas for the 39% of the site any project had been presented; on about the 12% of the contaminated spots remediation are working in progress. (Regione Veneto: Sezione Progetto Venezia, 2014). Concerning remediation applications, ISCO, MPE and ECRT techniques were proposed in the majority of the contaminated spots (D'aprile, 2007) due their in-situ working conditions; great limitations were found dealing with metal's remediation. According to different authors (Acar *et al.,* 1995; Li *et al.,* 1996; Mohamed *et al.,* 1997; Rosestolato *et al.,* 2015) metal's removal by electrochemical treatment could be considered as a consolidated practice dealing with lab and bench scale; scale up of the technique had been experienced on few applications (Wieckzorek *et al.,* 2005, Villen-Guzman *et al.,* 2015) and results were proved to be conflicting. The importance of speciation analysis on the contaminated soil seems to be a fundamental step in order to assess the feasibility of the ECRT application (Garcia-Rubio *et al*., 2011) that should be combined with accurate cost-benefit studies.

In this study, the feasibility of a pilot scale ECRT application for Mercury removal will be evaluated in light of the results given by speciation and cost-benefit analysis; in parallel, results and evaluations will be discussed taking into consideration the legislation context that seems to greatly limit the applicability of the technique.

PART 1: BACKGROUND ELEMENTS

1. PORTO MARGHERA INDUSTRIAL SITE

This chapter will focus on the history of Marghera and Porto Marghera, from the industrial rising on the early 20‘s to the dramatic current situation. Quoting Chinello (1975):

The developement of Marghera -which is the capitalist depevelopment of Venice and its harbor - is not a sudden event, neither does it start during the First World War nor at the end of the Second World War, but it has its roots further back in the previous century, all through the '800. It's a slow, devious, articulated and contraddicting process [...]

1.1 The dawn of Marghera

It seems useless to remind that through the ages Venice had based its economic predominance and its strenght on the surrounding lagoon; the heart of its power was the harbor, located inside the lagoon, among the canals, thus giving protection to warships and trade ships. From the early years of the 1800 this situation rapidly changed: under the French dominance significative variations of the flow of Canal Salso and the construction of Forte Marghera in the nearby area of the mainland were the first steps towards Venice‘s industrial future. Another key point for the industrial evolution of Venice – Marghera is the railway connection with the mainland that was almost completed in the 1850s. The railway gave the possibility of a stable and efficient link between Venice and the core of the industrial development Milan (Chinello, 1975). The relationships with the mainland had a great impact on the development of manufacturing sectors in Venice; it was of primary importance to have a direct connection with the Adriatic sea and at the same time treatments for the incoming good were required (Chinello, 1975). Should be underlined that, from the 1839, coal and oil were stocked in the harbor of Venice, being the most traded goods.

In the early years of _900 new spaces were required in order to fix the hygenic problems related to demographic issues, as well as to satisfy the increasing trade market that had almost saturated the ancient harbors and docks in the lagoon. Several projects in favour of the enlargement of the harbor were presented, as represented in the figure below, only considering the space inside the lagoon; on the contrary, the hypothesis presented in 1902, to take advantage of the soil on the mainland in the nearby area of the Mestre‘s municipality was a great innovation as the suggested territory included a land of almost only marshlands (Barizza, 2008)

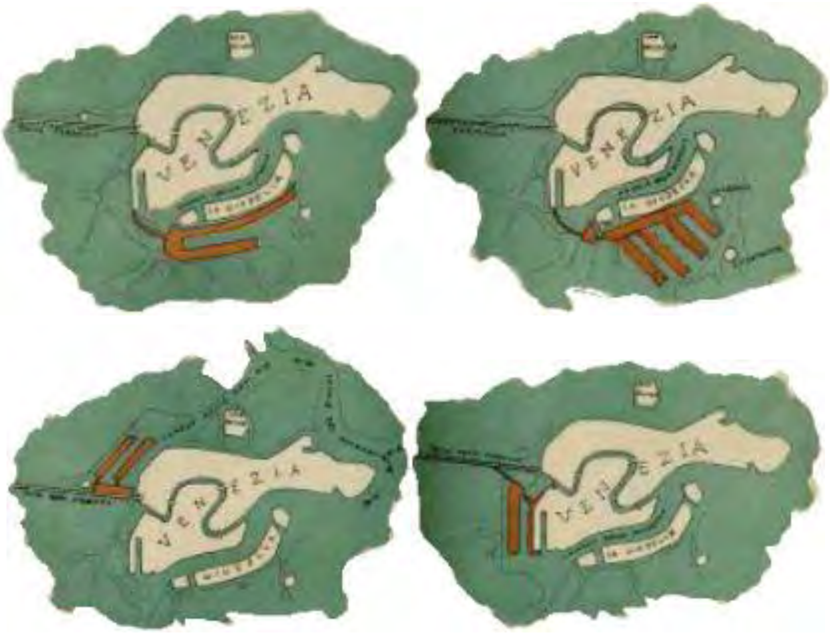


Fig .1.1 Enlargement of _La Marittima‘‘. Source: Barizza, 2008

Finally in the 1907 the Government‘s council disposed funds in order to complete the enlargement of the ancient dock (so called _*La Marittima*‘‘) and to start the creation of the –*bacino sussidiario ai Bottenighi*” as the inland dock (Chinello, 1975). Actually, it seems reasonable to say that that year was the beginning of the Marghera-affair.

The series of charts listed below (figures 1.2, 1.3, 1.4) demonstrate quite evidently the changes of the lagoon in the nearby of the docks in Venice and on the mainland, stressing out the gradual transformation from sandbanks to the actual industrial configuration of Marghera‘s harbor.

Fig.1.2 Lagoon‘s chart 1840, De Bernardi. Source: Atlante della laguna Cigno.

Fig.1.3 Lagoon's chart 1901, Genio Civile. Source: Atlante della laguna Cigno.

Fig.1.4 Hydrographic Lagoon's chart 1932. Source: Atlante della laguna Cigno.

As mentioned before, space demand was related also to demographic problems that were forcing on Venice since 1900; the project approved in 1917 did not only concern the industrial harbour but also a great residential area in the nearby of Marghera. Consequently, the social scenario in the proximity of Marghera deeply changed, people moved from the rural countryside to the industrial area looking for a stable workplace in the emergent industrialization scene.

Few years forward the lagoon scenario would have been changed forever being shattered by a severe overbuilding, the damages of which are hardly quantifiable. These changes were announced consequences of the ―Great Venice‘‘ project. A new arrangement of Venice boundaries was taking form; the historic city center was strongly exploited with shows, exhibitions and tourism, while the inland was fully designed to industrial activities and new residential areas. Consequently, from 1920 to 1950 populations passed from 20,000 to 90,000 inhabitants and from 5,000 to 25,000 for Mestre and Marghera respectively (Pozzan, 2014).

1.2 The rising of the industrial area

Even if the First World War stopped the activities for almost 48 months from the 1918, in the 1928 at least 60 industries were working in Marghera (Soriani, 2009). Thanks to several funds given by the government, the abundance of oil as source of energy and the increasing orders of the defense industry the harbor was growing widely; in the late 30‘s the First industrial area was employed by more or less 100 industries and 20,000 workers. So, quickly up to the late 30‘s, Marghera became the core of electrometallurgical, electrochemical and chemical industry. During the Second World War, Marghera was heavily bombed, looted and partially abandoned; in the late 40‘s the restart of all activities was limited by the loss of energy, material and even equipments (Pozzan, 2014).

Fig.1.5 Bombing on Marghera‘s Vetrocoke, 1944. Source: Pozzan, 2014.

Thanks to the high presence of manpower and the conversion of the major plant to chemical industry, in the first half of the 50's, the First industrial area was fully employed; once again new spaces were required. A schematic summary of the development of the area is reported in table 1.1 and in figure 1.6.

Tab.1.1 Development of industrial activities from 1920 to 1950. Source: Pozzan, 2014

Year	Surface occupied by industries (ha)	Number of firms	Number of employed	Maritime traffic (tons)	Railway traffic (tons)
1920	77	11	-	-	56,595
1925	198	33	3,440	211,763	275,266
1930	385	73	5,100	824,413	670,504
1935	480	84	10,120	1,605,503	660,975
1940	500	95	17,300	1,530,369	1,970,253
1945	528	103	15,700	159,183	64,917
1950	528	128	22,500	2,119,694	1,097,590

Tab.1.1 Development of industrial activities from 1920 to 1950. Source: Pozzan, 2014

Fig.1.6 1950's view of productive sections reconstruction. Source: Pozzan, 2014

Just a decade after the Second World War, the Second industrial area was almost completed and occupied by petrochemical activities. Unfortunately, the speed which the Second industrial area had grown had dramatic consequences for the environment; most of the land arranged for the new industrial area was composed of sandbanks filled up by toxic sludge, dredging sediments and processing slag of the First industrial area.

Fig.1.7 60's view of First and Second industrial areas. Source: Archivio Ente Zona Industriale.

Even though the Second industrial area hadn't been finished yet, the project of a third area located in Fusina, obtained by the filling with sediments coming from the dredging of new canals in 1963 was presented.

1.3 The sunset of Marghera

On one hand Marghera was reaching the highest point of its productivity trend (almost 250 firms and 30000 emplyed in the middle 60's), on the other the First industrial area started to show its own limits: equipment and processes of the early 50's were already passed in the last 60's and first sanitary problems appeared with the VCM-affair in late 70's. De facto, the 1973 could be considered the turning point of Marghera's development since any further enlargement of the area had been stopped by the approbation of a special law.

All things considered, it can be said that the early 80's were the beginning of the end for Marghera as a consequence of several reasons. The first years of 70's were the so called „oil crisis'' years, the principal source of energy was no longer available or at least economic; the working class's strikes caught the attention of media on the emerging sanitary problems and on the environmental impact of the almost overcoming industrial processes of the industrial corporations. At the same time more central cities as Padua or Vicenza were growing by more flexible strategy of inland ports and middle-industry power (Barizza, 2008). The increasing tourism on Venice of the 80‗s gave the final blow on Marghera; heavy industry was no longer the source of wellness as it was decades ago and it was no longer able to draw social consent.

Porto Marghera was told nothing else than an ‗history accident‘‘ and a bulky heritage of the great industrial and capitalistic modernity of Italy (Chinello, 1975).

Sadly, the recent story of the harbor is worldwide renowned for the high level of pollution both on soils and water and the related effects on the lagoon: in 1998 almost 6000 ha of the productive area were classified as SIN comprehending soil, canals and lagoon.

2. ITALIAN LEGISLATIVE FRAMEWORK FOR CONTAMINATED SITES

It is worthy to spend a quick focus on the Italian legislation about remediation sites in order to better understand the legal context of Porto Marghera. The content of this chapter had been developed thanks to the review of ARPAV documents, lesson material given by Prof. Butti and legal text from Bosetti-Gatti web site.

2.1 First Italian guidelines: D.Lgs. n. 22 /97

Actually the first step on remediation legislation was introduced just in 1997 by art.17 of the D.Lgs.22; well known as Ronchi Law, this code introduced two fundamental concepts of responsibility and subsidiarity. The first notion is related, as nowadays, to the Italian expression *‘‘who pollutes have to pay’’* and it is well described in the second comma of art.17 as follow:

„*Anyone who, even accidently, causes the exceeding of limits [...] have to proceed, at its own expense, to the remediation, the securing of the area* …‘‘ (D.Lgs.22/97; art.17; comma 2)

In parallel with the responsibility concept, the subsidiarity notion gave a hierarchy on the remediation duty if the responsible of the pollution could not be found or could not be able to remediate. Subsidiarity concept could be explicated in the following 3 and 9 commas:

„*Individuals or public entities that, during their own functions, founds sites where pollution levels are higher than the prescribed limits, have to communicate to the Municipality to the Province and to the Region*.‘‘ (D.Lgs.22/97; art.17; comma 3)

„*If responsible do not provide to remediation or could not be found…remediation actions and securing are performed by the Municipality or the Region*.‘‘ (D.Lgs.22/97; art.17; comma 9)

A great new that was introduced by the Ronchi Law was the formulation of a standard scheme that could be applied on every site (D.Lgs.22/97; art.17; comma 1). In particular by the first comma were given the definitions of:

- Acceptability limits for soil, superficial and ground water as a function of their own intended use;
- Procedures of sampling and analysis;
- General criteria about securing, remediation and environmental restoration of the polluted site.

2.2 Technical regulation for contaminated sites: D.M. n. 471/ 99

Following the line given by the Ronchi law in 1999 was introduced the D.M. 471 as an application of the European concept of ‗command and control''. Many remediation campaigns, involving also Porto Marghera, are still running under the prescription of the decree 471/99; it is of primary importance to understand its key points. The decree 471/99 could be seen as an implementing decree of the law 22/97 as it gave a standardized and practical method for procedures and arrangements for securing, remediation and environmental restoration. The great innovation was that the decree 471/99 is a procedure based on a quality criteria in function of the so called acceptable limit concentrations (*VLCA Valori Limite Concentrazione Ammissibile*); at the same time a series of new definitions were introduced (D.M. 471/99; Art.2):

- Site: defined and delimitated area of different environmental matrices comprehending possible buildings or plants ;
- Potentially polluted site: area subjected by past or present anthropogenic activities characterized by the possibility of the presence of harmful pollution on soil or water.
- Polluted site: area where concentrations of the pollutants are higher than the acceptable limit concentrations in soil or water.

Should be underlined that the definition of polluted site takes into consideration the exceeding of just one among all the parameters to be considered polluted; on the other hand the definition of potentially polluted site is related to the consequence of an event that may had polluted the site.
Of greatest importance was the introduction of the above mentioned acceptable limit concentrations as the threshold values of the polluted site concerning soil, superficial and ground water. These values were considered to be different as a function of the soil-site‗s intended use and they may undergo to some exceptions. For acceptable limit concentrations there are derogation related to the concepts of:

- Natural concentration of the soil: the natural concentration could be used as the acceptable limit concentration if it is higher than the acceptable limit concentration listed in Annex 3 (D.M. 471/99; Art.4; comma 2);
- Residual concentration and BATNEEC: if the acceptable limit values could not be reached even using the best available techniques not entailing excessive costs and the risk analysis ensures satisfying measures of safety, the polluted site could be restored using proper securing measures (D.M. 471/99; Art.5; comma 1).

On the other hand, concentrations lower than the acceptable limits concentrations are prescribed for a list of areas of particular concern like sensitive areas (*''Aree Sensibili''*) listed among the decree 152/99) and areas devoted to drinking water capitation (D.M. 471/99; Art.4; comma 3).

If on one side the acceptable limit concentrations quality method is the strength of 471/99 on the other hand it shows a considerable lack of flexibility. In fact, by the Art. 2 definition of remediation is evident that the aim of the operations is to get concentrations lower than the acceptable limit concentrations; on the contrary, any specification is reported on the kind of pollutants, on the form it is present on the soil or water and on its speciation. Referring to limits concentrations just with total concentrations is a huge limits for the assessment of the remediation in terms of efficiency and in terms of law‘s requirements fulfilling. This limitation of decree 471/99 will be the key point of the next chapters dealing with Hg concentrations in soil. It is worthy to underline the meaning of the term ‗securing‘‘, frequently used among the above mentioned commas and definitions. This term assumes different shades as a function of the aims of the action, the duration of the securing measures, remediation efficiencies and acceptable limit concentrations.

In general, Art.2 of decree 471/99 decree defines safety measures as the set of actions, limitations and monitoring campaigns aimed to prevent harmful effects, from contaminated sites, on environment or public health. Once a contaminated site has been identified safety measures get the connotation of emergency securing as they act rapidly in order to prevent, reduce or remove the source of contamination waiting for remediation or permanent securing measures. On the contrary, once a contaminated site has been identified but even with BATNEEC is not possible to remove the source of contamination, safety measures get the connotation of permanent securing. Their aim is to definitely isolate the source of contamination by limitations, controls and monitoring campaigns. Due to the frequent references to the different step of projects in next chapters, in figure 2.2.1 is reported a scheme representing the decree 471/99 procedure concerning remediation‘s projects.

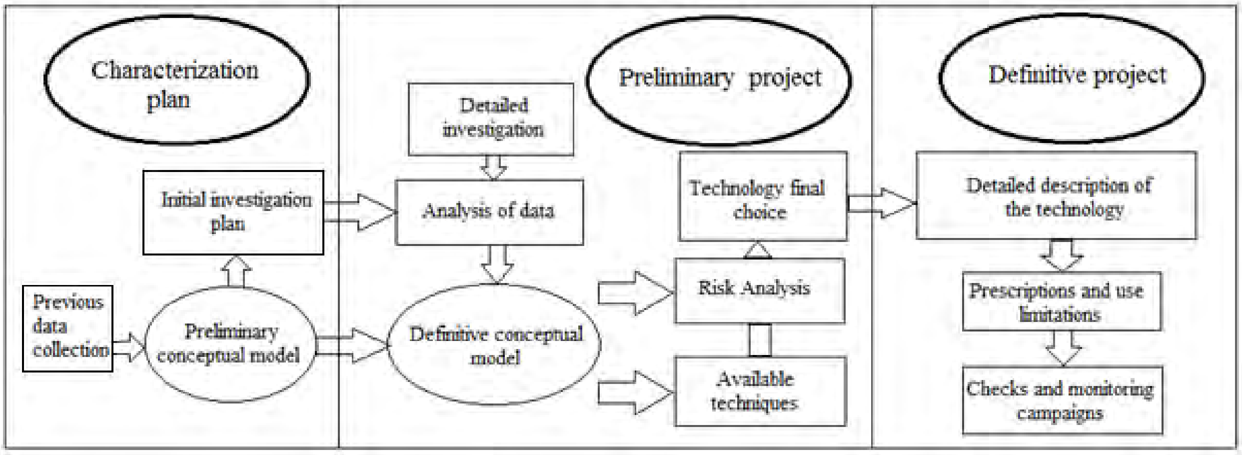


Fig. 2.2.1 Graphical representation of 471/99 project‘s steps.

2.3 The new legislative framework: D.Lgs. n. 152/06

Nowadays environmental legislation referred to the D.lgs. 152/06 called ‗Testo Unico‘‘, as the transition from decree471/99 to this code is still running it is of great concern understand the changes between the two texts. First, the 152/06 is based on a risk analysis quality criteria instead of just limit concentrations. More precisely, it combines the two criteria into a multistep procedure based on both limit concentrations and risk analysis results. The framework of the procedure is similar to the decree n. 471/99 but few important differences contained in Art. 242 should be underlined:

1. After a potential contamination of the site, the investigation is performed to assess the CSC the exceeding of these concentrations does not mean the site is contaminated, the site is defined as potentially contaminated. CSC work as ‗warning concentrations‘‘ not as limits as VCLA.
2. The site is defined as ‗contaminated‘‘ if the measured concentrations exceed CSR calculated by risk analysis tools. CSR are the object of the remediation campaign.

It should be underlined that risk analysis results of CSR of 152/06 are usually higher than values of VCLA introduced by decree 471/99, so it seems to be reasonable to say that the CSR underestimate the contamination of the site. On the contrary, due to the high quantity of samples required for the risk analysis tools the decree 152/06 had become a more flexible and realistic procedure. Limits concentrations and thresholds values concerning water quality are referred to D.lgs 152/99 in both 471/99 and 152/06.

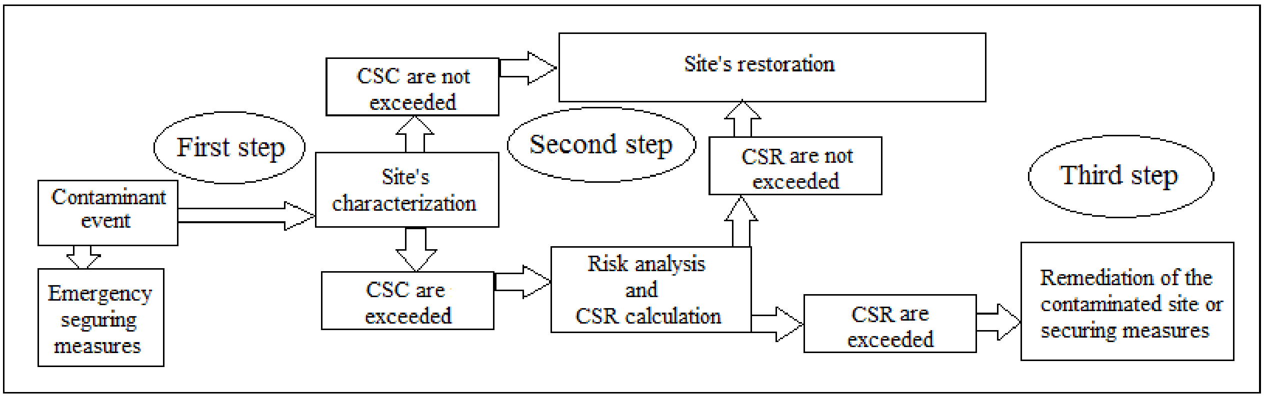


Fig. 2.3.1 Graphical summary of Decree 152/06 framework‘s steps.

2.4 Site of National Interest: SIN

Dealing with Porto Marghera other Italian environmental regulations must be mentioned due to the high specificity of the site and its national relevance. As previously mentioned, lists of contaminated sites were set with Ronchi law and both 471/99 and 152/06, but of great concern is the institution of a list of national interest sites classified as SIN. The definition as SIN depends on the site‘s and pollutant‘s characterization, the possible environmental and social impacts. Driving criteria for the evaluations of SIN are (D.lgs. 152/06; Parte quarta; Art.252; comma 1):

- Areas of high environmental quality maybe present;
- Areas affected by an high risk for human health or environmental quality;
- Areas of relevant socio-economic impacts ;
- Areas comprehended between different regions.
- Areas in which remediation plans are set on D.lgs. 42/04

Through the years SIN sites had been bounded by different laws, however it is possible to say that the first law about SIN institution was the 426/98 where 16 SIN were identified.
The management of these sites, unlike other contaminated sites, is consigned to *Ministero dell'Ambiente e della Tutela del Territorio e del Mare* (MATTM) that involve also municipalities and regions. Nowadays 57 site are classified as SIN covering an extension of almost 2% of Italian national surface. Details about SIN of Porto Marghera will be presented in the next chapters.

3. AGREEMENT PROGRAMME FOR CHEMISTRY & MASTER PLAN

Going into details of Porto Marghera reality, in parallel with the definition of SIN, was signed the *Accordo di programma per la chimica*, approved in 1999. The need of a programmatic text for the recovery of Porto Marghera was of primary importance not just for manifest environmental problems but also for economic and social reasons. The whole area, in addition to the high levels of diffused pollution, presents evident signs of urban decay, lot of abandoned or underexploited installations and lacks of primary infrastructures. However, as written in the text, Marghera was still seen as ‗the key point of Italian chemical industry to be restored and oriented to rigorous and environmental respectful guidelines''.

Moreover, the aim of constitute and maintain optimal conditions for coexistence between environment and chemical industry was planned to be achieved by:

- restoration, safeguard and remediation of sites combined to safety measures and risk prevention in order to make possible the coexistence between industrial and residential areas;
- reduction of the emissions to the atmosphere and lagoon by the conveying of waste water and run off water to an equipped treatment plant and in parallel by the creation and restoration of green areas in the nearby of the lagoon and on the mainland;
- innovation, competition and employment in the area by the valorization of the harbor and channel digging, dismantlement of the abandoned plants and the use of the best available technologies to guarantee economic profit and environmental safeguard.

One of the product of above mentioned text is the SIMAGE (*Sistema Integrato per il Monitoraggio Ambientale e Gestione Emergenze*), set up in order to manage industrial risk situation and emergencies in case of accidents. The need of a ready-to-use tool able to manage in short time authorities and population was of primary importance due to the fact that in the 90's were still presents:

- industries classifies by Seveso Directive of high risk;
- movement of risky substances by rail, by road and ship;
- industrial area in the proximity to dense populated areas.

In response to these issues, continuous monitoring of pollutants in different matrices were developed, at the same time management of emergency situations was set up in combination to rail, road and ship traffic monitoring. The whole system was integrated by the capacity of quick public information. The agreement program was such a wide remediation and restoration plan that, in 2000, was integrated by a more technical and practical act called the Master Plan. The aim of the integrated text was to coordinate and harmonize the contaminated site respectively taking into consideration the whole restoration of the area, and on the other side considering for each specific case the best economic and technical solutions. In other words the Master Plan works as an individuation and planning tool for the remediation actions on Porto Marghera. Looking at the contents of the act, the above mentioned aim could be split by a series of other steps. In particular: the definition of a complete and accurate cognitive framework about the status of contamination into the different matrices; the definition of the most technically and economically suitable remediation techniques; the technical solutions and the management for storage, treatment and disposal of remediated materials; the time-planning for the operations; a cost analysis; the guidelines for the monitoring of Master Plan‘s development; the guidelines to combine coherently public and private operations. Through the years, concrete results of the Master Plan could be seen in the subdivision of Porto Marghera into macro-island of interest and at the same time the conveying of the waste water to the enhanced treatment plant of Fusina. At the same time actions of permanent securing of the border of the area between soil-lagoon and soil-soil surface had been developed by the sheet piling system.

Fig. 3.1 Macro island boundaries and sheet piling work in progress. Source: Master Plan, 2000

In fact, it should be underlined the critical issue concerning the framework of channels in Porto Marghera; high levels of pollution had been demonstrated both on sediments and water in the Northern channel as well as in the Lusore-Brentella channel. Since 1998 the programmatic framework had been renewed in order unlock the standing off situation that has been creating along years of fuzzy bureaucracy. However, it should be reminded that the presence of so many different activities and the participation of several private actors, make the process of homogenization of the whole remediation campaign more difficult and slow. Nowadays could be stated that the characterization plan of the SIN is almost concluded and at the same time project for permanent securing or remediation had been at least presented; for wide areas, projects of remediation had been also approved and executed. Until 2012, sheet piling could be considered to be developed over the 50% of the entire perimeter on the other hand the remediation campaigns in terms of projects and operations still presents low percentages on the whole activities to be done. Until 2013, from data given by MATTM, percentages concerning public mainland are in the order of 10.3 % emergency securing measures, 81.4% presented characterization plans, 74.7% characterization result shown, 43.6% presented remediation plans, 28.0% approved remediation plans. Recently (2013), as reported in figure 3.2 the whole SIN undergone to a new delimitation that involves just industrial areas. This new configuration, that excludes residential, agricultural and lagoon areas, was desired in order to speed up and simplify the remediation procedures.

Fig. 3.2 Red line SIN 2000 boundaries, Yellow line SIN 2013 boundaries. Source: Regione veneto, 2015

4. DESCRIPTION OF THE SELECTED SITE

In this chapter will be given a detailed description of the area of interest that comprehends the study case contaminated site. General information about geology and hydrogeology will be reported while particular stress will be given on environmental characterization of both soil and groundwater. The whole area is located on the first industrial area of petrochemical activities, it covers an area of almost 120 ha bounded by a perimeter of almost 6 km. The delimitation, given by the ‗macro-islands‘‘ definition on the Masterplan, bounds the area on its southern, eastern and western part with the Lusore-brentella industrial canal, while on the northern part with a commercial district.

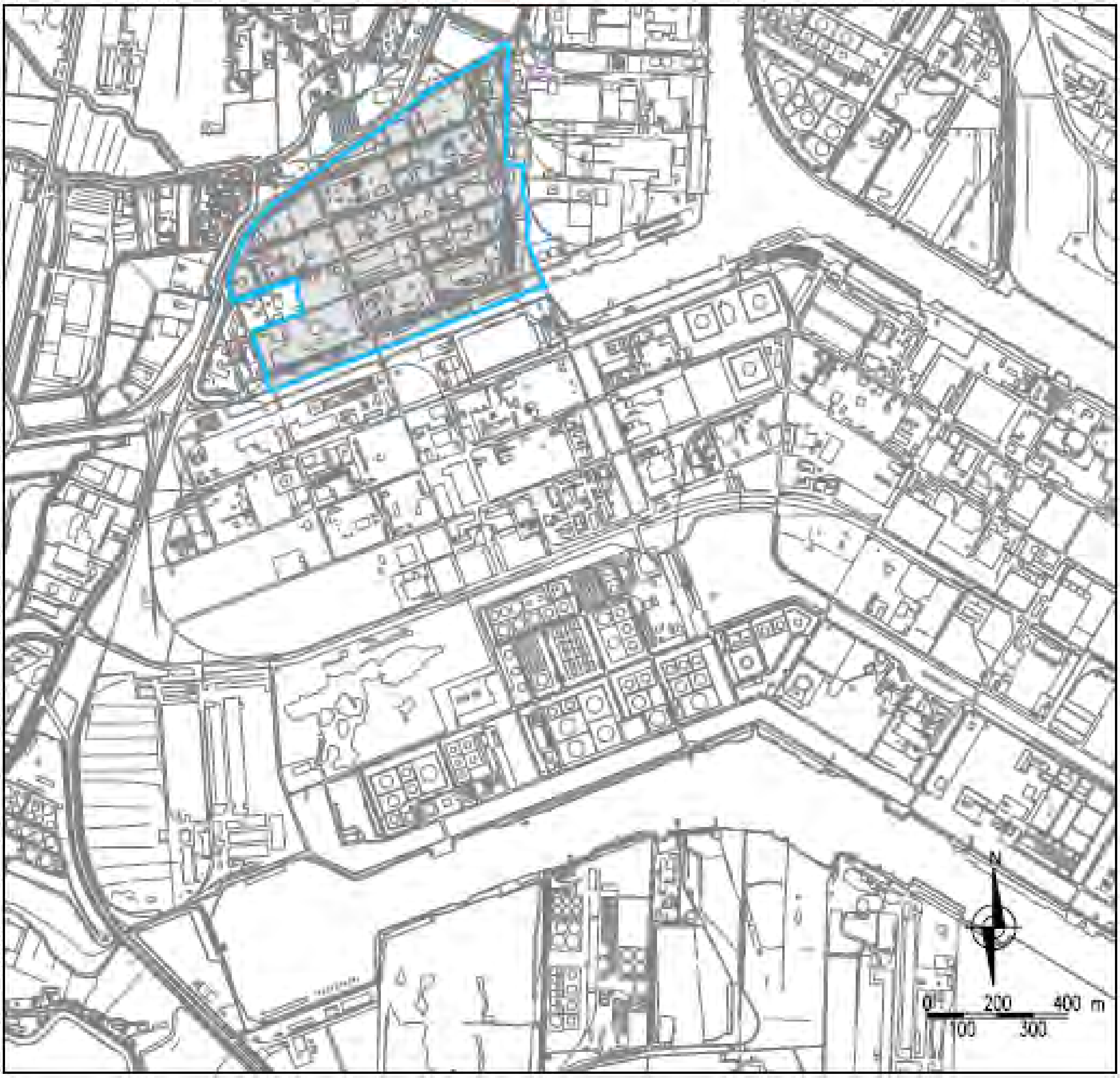


Fig. 4.1 BON PM 185 boundaries (blu line). Scale 1:20000. Source: Risultati caratterizzazione integrativa (Set 2005) Syndial.

4.1 Geological and lithological characterization

At a first sight, the whole area shows an homogeneous and flat morphology characterized by quotes in the range of 2.3m to 3.7m s.l.m. On the contrary, results of the geognosthic perforations had demonstrated a more heterogeneous composition of the soil. Anyhow, as it is presented in figure 4.1.2, it could be stated that a general stratigraphy is present all around the area and it may be summarized into an alternation of granular sandy material and cohesive clayey layers combined with the presence of silt materials.

Fig. 4.1.1 _Sezioni stratigrafiche‘‘ particular. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

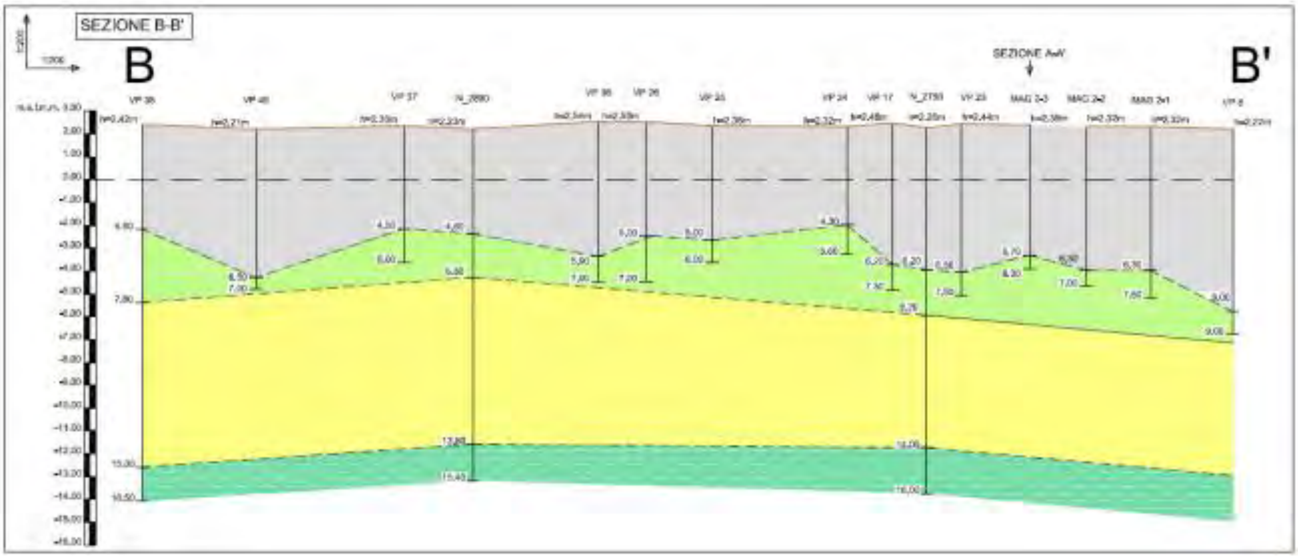


Fig. 4.1.2 _Sezioni stratigrafiche‘‘ particular. Grey area: backfill soils, Green area: clay, clayey silts and peat , Yellow area: sandy deposits, Blue area: clay, clayey silts and peat. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

More in details, from the top to the bottom, the different layers may be distinguished as:

1. Heterogeneous, backfill soils and material: from top soil quote to 3.1-9.3 m depth, of an averaged thickness of 5.5m. It is composed by sandy material mixed to cobbles, gravel, clay, silt and organic materials. Not infrequently this soil had been replaced and added with residues and processing by-products of the First Industrial area.

2. Clay, clayey silts and peat: defined as the top impermeable layer, it goes, uniformly all around the area, from 3.7 – 7.8 m to 9.2 – 12.5 m under the top soil quote. This layer, of a averaged thickness of 4.6 m, is composed by gray-brownish colored clays mixed with few percentages of silts; compact clayey silts mixed with few percentages of sands; brown peat of silt and clayey nature.

3. Sandy deposits: of an averaged thickness of 5 m, this layers could be found, uniformly, from 6.7-11.7 m to 14-16.2 m. Defined as the first aquifer, this layer is composed by fine grained gray sands with few percentages of silts. Of great extent are the discontinuities formed by clay and clayey silts.

4. Clay, clayey silts and peat: defined as the secondary impermeable layer, this layer has never been fully characterized. Anyhow, thanks to past studies, it could be stated that it has a variable extent from 1m to 8 m, below the 14–16.2 m from the top soil quote. Its composition is mainly characterized by gray silts and clayey silts.

4.2 Hydrogeological characterization

Strictly related to the soil composition, even if the presence of discontinuities of great extent are frequent, the hydrogeological behavior of the area could be described with a good approximation. In particular, the groundwater hydraulic system could be assimilated to a multilayer composition of two aquifers. At the same time, it should be underlined that water table levels are sensibly affected by the series of pumping actions of the securing measures. The two hydraulic bodies, from top soil to 18-20 m of depth, are confined within layers of low permeability. More precisely they could be identified as:

- a series of superficial permeable layers, of an averaged extent of 5.5 m, confined on the bottom by the impermeable horizon in correspondence of the end of the backfill layer. The behavior of this hydraulic body, that could not be properly defined as an aquifer, is essentially related to the fluctuation of rainfalls that saturate the most permeable top material. The water table levels are in the ranges of a minimum of 0.8m to a maximum of 2 m above the sea level.

In terms of hydraulic conductivity, due to the high heterogeneity of the soil matrix, sensible variations are present. Moreover, due to the presence of fine particles, it could be stated that permeability and filtration coefficients are almost negligible and mostly in function of rainfalls.

- an alternation of sandy and mixed layer, of an averaged extent of 5 m, confined by the top impermeable layer and the second impermeable layer. Differently to the superficial hydraulic body, this aquifer, due to its boundaries , works in pressure. Salty water interferences occurs. The water table levels are in the ranges of a minimum of 0.2m to a maximum of 1.2 m above the sea level. In this case permeability coefficient are in the ranges of 10^{-5} m/s.

On the contrary, from results of in situ tests, impermeable layers are characterized by ranges of hydraulic conductivity from10^{-9} to 10^{-7} m/s. Sampling points used on the above mentioned characterization will be detailed discussed on chapter 6.

4.3 Ancient activities and sources of contamination

In this chapter will be presented a brief summary of the plants that were working, from the 50's, on the First industrial area _Vecchio Pertrolchimico'' in order to assess the most probable sources of contamination on both soil and groundwater. Particular stress will be given to Chlor-alkali and VCM plants, respectively related to Mercury soil's contamination and to chlorinated compound water contamination. A brief presentation of the whole set up of CV and CS plants that had been working on the area is given in the table below in order to have a first, general approach to the complex framework of the ancient industrial area.

Tab. 4.3.1 Set up of CS,CV. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial

Plant	Production	Start	End
CS3	Cloro-soda-hypochlorite	1951-52	1972
CS4	hypochlorite	1951-52	1994
CS5	Liquid chlorine	1951-52	1974
CS5	Liquid chlorine	1956	1994
CS7	Soda concentration	1951-52	1990
CS7	Soda concentration	1960	1991
CS11	Muriatic acid	1954	1981
TR1-2	Tri/tetrachloroethene	1951-54	1991
TS1-2	Trichloroethene	1951-54	1991
TS1-2	Trichloroethene	1951-54	1991

TR4	Tetrachloroethene	1957-60	1991
PA1	Plasticizers	1953	1967
BC1	Chloromethyl	1957	1998
CV1	VCM	1951-54	1970
CV3	PVC	1951-54	1970
CV5	PVC granules	1953	1990
CV6	PVC emulsion	1956	1989
CV8	PPB	1956	1989
CV11	VCM	1958	1985
CV10	VCM	-	1985
CV14	PVC suspension	1958	1986
CV15	PVC granules	1960	1990
CV16	PVC suspension	1958	1986

4.3.1 Chlor-alkali line

As intermediary step of the PVC line, the Coro Soda plants produced, until the 90‘s, caustic soda and chlorine. Briefly, the Mercury cells Chlor-alkali process could be summarized into:

1. flow of 35 % concentrated brine solution into an heated sloped cell at 60° C;
2. the inducted current forced the following reactions on the electrodes:

$$2Cl^- - 2\,e^- \rightarrow Cl_2 \qquad ; \qquad Na^+ + Hg + e^- \rightarrow NaHg$$

3. the depleted brine goes out from the cell as solution;
4. the chlorine gas get blown on the top of the cell;
5. the Mercury enriched amalgam goes out from the cell and sent to a secondary tank;
6. Mercury is recovered from the secondary tank by the use of Fe or Ni catalyst thus causing the separation of H gas and caustic soda concentration.

This kind of cells, usually used as 100 cells in parallel, are wide but shallow tanks of approximately 15m width, 2 m length and 0.3 m height. Anodes made of graphite or DSA are disposed parallel to the bottom Mercury cathode of almost 1 cm from the bottom. Energy required varies from 180,000 and 315,000 A.

4.3.2 Chlor-alkali departments

In particular, the mean feature of Chlor-alkali line of the First industrial area (CS3) comprehends:

- an incoming plant of crushing, weighting and dealing of rock salt e marine salt;
- 10,000 tons capacity stores;
- concrete and ebanitated iron open air tanks for the brine preparation;
- electric switching room from alternate to direct current by the use of rotating groups and Mercury-gas rectifiers;
- electrolytic room composed by 128 Mercury-cathode cells.

At the end of the line a series of steel tanks (two tanks of 500 m^3 each and two tanks of 250 m^3 each) were used for the caustic soda storage; blowers and compressors for the aspiration and liquefaction of Chlorine gas and Hydrogen gas. However, it will be useful, especially for the next chapters, to build up the past Chlor-alkali framework on the area in order to be able to understand or verify the possible source of contamination. More in details, in addition to the above mentioned CS3 department, the past Chlor-alkali framework comprehends:

- CS4: sodium hypochlorite production department. Briefly, the process was based on the chlorine absorption on a 20% hydrated sodium solution. In parallel, CS4 was used as storage department of hypochlorite, soda solution and chlorinated water. Respectively 4 tanks of 32 m^3 each, 2 tanks of 32 m^3 each and 2 tanks of 20 m^3 each , 1 tank of 20 m^3 were used.

- CS5: liquefied chlorine production department. Developed on two different lines, was able to produce liquefied chlorine first by using chlorine gas, Freon 12 and later on by using chlorine gas, Freon 12 and Nitrogen. Chlorine gas was provided by the CS3 department and condensate by Freon 12 refrigerators circuits. Two chlorine‘s storage tanks of 33 m^3 each were present at the end of the line.

- CS5/D: liquefied chlorine distribution department. From 8 tanks of a total amount of 65.5 tons, the liquefied chlorine was sent to the downstream chlorine-consumers departments.

- CS7: concentrated caustic soda production department. Developed on two different lines was able to produce soda caustic from 2 step-process of a sequence of heating and concentration reactions.

- CS11: muriatic acid production department. The aqueous solution was obtained by the abatement with water of the incoming HCl gas; the organic vapors, once condensate, were discharged in the sewer.

As could be seen in table 5.1, any of the CS plants of the First industrial area are still working; from the 70‘s the whole CS production had moved to the Second industrial area with the CS23/24/25 departments. The location of the different CS departments is given in figure 4.3.1 in the end of this chapter.

4.3.3 Chlor-alkali environmental impacts

It should be underlined that, in Chlor-alkali plants, the Mercury cathode cells are nowadays considered to be an overcome technology due to the high unlikely environmental effects. In particular, by the European directive on IPPC, Mercury cathode cells should be substituted by membrane cells, considered to be less energy consuming and more efficient. At the same time, by the use of membrane cells Mercury will not be present in any form during the process thus removing the possibility of liquid or gaseous Mercury spills in the environment. Evidences of the environmental effects of Mercury are known since the 50‘s due to the high levels of intoxications in Minamata in Japan. The behavior of Mercury in the environment, like other metals, greatly depends on its oxidation or reduction state; It may be present as Hg^{+} , Hg^{2+} or forms of organic Mercury as a result of the methylation process. As it had been reported by Rani *et al.*, 2011 the methylation process is of great concern dealing with the eco toxicological characteristic of Mercury. The reason is related to the fact that the bioavailability of Mercury after methylation is significantly higher than the other forms; studies had found that almost the 80-95 % of Mercury in fishes is present as Methyl-Mercury. The bioaccumulation of Methyl-Mercury in the trophic chain of fishes is of extraordinary importance thinking that the adsorption in gastrointestinal tissues is closed to 95%. Moreover, Mercury effects on human body affects also immune, nervous and renal system with great effects also on fetus.

4.3.4 Vinyl chloride line

The further step in the PVC line is the production, by different processes, of the vinyl chloride monomer (VCM). VCM is one of the leading chemicals in PVC production and it is worldwide mostly used for this purpose and in a little part for solvents production. The series of step that composed the VCM to PVC process is quite complex and articulate; therefore will be reported just the key points and a brief description of the two technologies that were present in Marghera until the 70‘s and the 90‘s.

For many years this VCM production from acetylene had been the most used technique thanks to its simple and robust framework, more recently it has been abandoned due to its high raw hydrocarbons requirement and Mercury catalyst presence. The gaseous process, based on an exothermic reaction between hydrochloric acid and acetylene in presence of a mercuric chloride catalyst, could be summarized as follow:

$$CH{\equiv}CH + HCl \rightarrow CH_2{\equiv}CHCl$$

It should be considered that, thanks to the presence of HCl, from intermediary mercuric chlorine-Vinyl Chloride is possible to the vinyl chloride monomer and, in parallel, the regeneration of the $HgCl_2$ catalyst. Once again, the presence of Mercury during the reactions had considerable environmental consequences as it will be demonstrated on next chapters dealing with the characterization of soils.

On the other hand, VCM production from DCE cracking was based on the endothermic reaction of decomposition of Ethylene Dichloride at considerable temperatures between 400-500°C:

$$CH_2Cl{-}CH_2Cl \rightarrow CH_2{=}CHCl + HCl$$

As other cracking processes, significant amount of by-products are formed during the reaction; in particular it should be underlined the production of:

- Hydrocarbons: Ethylene, Benzene, Butadiene;
- Chlorinated derivatives: Chloroform, methyl-ethyl chlorides;
- Dehydrochlorination derivatives: tri-tetra-pentaChloroethane, perChloroethane.

4.3.5 VCM departments

Concerning the past framework on the first industrial area, that could be seen in figure 4.3.1, it should be underlined the presence of the following departments:

- CV1, CV10: HCl and VCM production department (from acetylene process). In CV1 line, the hydrochloric acid was obtained from the combustion between Hydrogen and Chlorine gas; a part of the HCl produced was watered to produce the HCl solution to be sold while the other part was combined with acetylene to produce VCM. The liquefied VCM was stored into 6 tanks of a total amount of almost 150 tons. On CV10 line the gaseous hydrochloric acid was fed by the cracking step of the downstream CV11. Once again, HCl reacting with acetylene in combination with catalyzers, VCM production was performed and stored in steel tanks.

- CV11: HCl and VCM production department (from EDC cracking process). EDC was provided by boats from the plant of Mantova; the line was equipped with: crude EDC storage (1200 m^3), cracking ovens, intermediary storing facilities (700 m^3), distillation and correction columns, distilled EDC storing tanks of 200 m^3.

- CV3, CV6, CV14, CV16: PVC production department. The lines, of few years of difference, were both fed with the VCM from CV1 department and the use of catalyzers was required. The substantial difference between the two regard the process itself: CV3,CV14 and CV16 departments used the suspension process for the PVC production thus to obtain a resin that had to be heated and dried; on the contrary, CV6 department used the emulsion process for the PVC production. On CV6 line, the polymerization of PVC and the storage of the intermediary emulsion were respectively performed on 8 autoclaves of 15 m^3 each and 8 tanks of a total amount of 125 m^3 each.

- CV5, CV15: PVC granules production. Of few years of difference, this two lines were based on the mix of the dusty PVC with other resins, plasticizers and dyes and the further heating of the mixture that had transformed into plastic. Finally the product get cut or crushed and packed.

- CV8: PPB production department. This compound was produced just for the VCM suspension polymerization. The line comprehends a series of heating and cooling tanks in combination to PPB polymerization plates and storage tanks.

To be more effective, the main features of the PVC line may be summarized as follow:

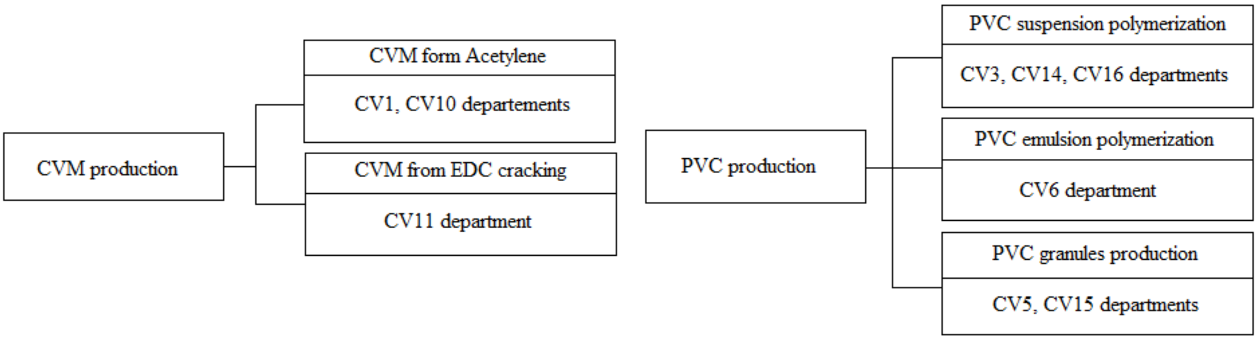


Fig. 4.3.5.1 Graphical representation VCM-PVC departments of the first industrial area from the 50‘s to 90‘s.

It should be mentioned that, like in the case of CS plants, any of the above mentioned departments had been working later than the first years of the 90‘s. Nowadays, the VCM production had been moved to the CV22 department while the PVC production is related to CV 24/25 and SINCRON 1. Since the 70's EDC has been produced in the CV23 facility.

4.3.6 VCM environmental impacts

The following brief description of VCM and analogue organic chlorinated compounds will be useful on next chapters of analysis results in order to verify and criticize any possible conclusion; the whole set of data was taken from Toxnet web site.

Vinyl chloride monomer is a colorless and sweet odor gas (at ambient temperature), characterized by a solubility in the ranges of 2,700 mg/l and vapor pressure at 25 ^{o}C in ranges of 2,980 mm Hg. Concerning partition coefficients, the following values should be taken into consideration:

- $k_{oc} = 57$;
- $\log k_{ow} = 1.36$;
- Henry law's constant = 2.78×10^{-2} atm m^3/mole.

Following the literature experiences it could be stated that VCM is expected have a great mobility in soil and volatilization from moist soil surfaces is considered to be a driving fate process. In particular it had been experienced that volatilization half live were in ranges of 0.2 to 0.5 days in function of the depth on soil matrix. On water environment VCM is unlikely to get absorbed on sediments ; while volatilization from water surface is likely to be a considerable fate process. Authors estimated volatilization half live of 2 hours and 3 days respectively for model rivers and model lakes. Had been demonstrated that VCM is susceptible to both abiotic and biotic degradation; in particular, photo chemically degradation at gas phase seems to be an important abiotic pathway; on the contrary, once get in solution, hydrolysis does not seems to be an effective reactions. Concerning biotic degradation of VCM several studies had been performed on both aerobic and anaerobic conditions; had been demonstrated that under aerobic conditions the biodegradation of VCM is possible and could combine both high efficiency and short time period. Anaerobic biodegradation is of greater concern because it is a process (reductive dechlorination) that had been demonstrated to be effective not just to vinyl chloride but also to higher chlorinated compounds. However, it should be underlined that further reductive dechlorination of VCM to ethylene is considered the great limiting step of the process and usually associated to vinyl chloride accumulation. Moreover, it should be reminded that in addition to direct sources of VCM contamination, vinyl chloride could be found as an intermediary product of tetrachloroethylene of trichloroethylene reductive dechlorination on contaminated sites. BCF values for algae and fishes (40 and 10) suggests that VCM is unlikely to be bio accumulated. It should be underlined that VCM‘s manufacture had been a frequent topic regarding environmental pollution and worker‘s safety. Through the years, since the early 60‘s, evidences of the carcinogenetic properties of VCM were validated all around the world by scientific committees (1964, Goodrich di Louisville (Kentucky), 1969 Michigan University Institute for Industrial Health, 1970 Doc. Viola, Cancer Research). Later on, just on 1973, the World Health Organization (WHO) confirmed the carcinogenic properties of VCM.

4.3.7 Chlorine line secondary departments

In addition of the above mentioned plants on the Chlorine line, other few plants must be mentioned. TR1, TR2, TR4,TS1, TS2 were departments assigned to the Tetrachloroethane and trichloroethylene production. In particular, Tetrachloroethane was produced by the combination of Chlorine gas, taken from the above mentioned plants, and the Acetylene in the presence of an Iron catalyzer (TR4). On the contrary, trichloroethylene was produced from thermal scission of the Tetrachloroethane in presence of an activated carbon catalyzer (TS1-2). TR1-2 plants were able to produce both Tetrachloroethane and Trichloroethylene with a store made of 3 tanks of respectively 800, 500 and 250 m^3. Concluding, BC1 department was assigned to the Benzyl Chloride production by using Chlorine gas and Toluene; the product of this process was used in PA1, PA2 facilities thus to synthetize plasticizers.

4.3.8 Other lines

To be thorough, in this paragraph a quick description of the other lines that were present in the area will be reported. First, a summary of the facilities is given on table 4.3.8.1:

Tab. 4.3.8.1 Set up of production plants . Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial

ACETIC ACID AND ACETATES LINE			
Plant	**Production**	**Start**	**End**
AC1	Acetylene from methane	1960	2002
AC2	Acetylene from carbon	1951-52	1970
AC3	Acetylene from poor gas	1953	1981
AC4	Ethanal	1953	1964
AC5	Acetic acid	1953	1989
AC7	Storage	-	-
AC8	Acetic anhydride	1955	1972
AC9/A-B	Butyl acetate	1953	1992
AC9/A-E	Ethyl acetate	1954	2001
AC11	Vinyl monomer acetate	1957	2001

AC14	MEP	1958	1961
AC12-16	Polyvinyl acetate	1957	1984
INORGANICS LINE			
AM1	Ammonia	1954	1977
AM4	Ammonia solution	1954	-
AM5	Sodium carbonate	1956	1991
AM6	Nitric acid	1955	2002
CYANIDES LINE			
AM8	Sodium/Potassium cyanide	1960	1998
AM10	Acrilonitrile	1960	1974
AUXILIARES SERVICES			
AL2	Liquid air/oxygen/nitrogen	1958	-
SA1	Thermoelectric station	1951	1976
ISOCIANATES LINE			
TD2	Carbon oxide	1971	2002

Plants of the acetate‘s line had been producing acetylene from methane, calcium carbide and poor gas from cracking processes. These kind of processes, beside requiring considerable amounts of solvents, were related to strong gaseous emissions from flares and abundant production of wastewater and muds. On the same line were produced also Vinyl Acetate, Acetic acid and Acetaldehyde by the use of strong acids and Mercury-iron catalyzers. An entire department was assigned to the storage of Acetic acid, Sulfuric acid, waste water and Vinyl Acetate. Departments assigned to this line where: AC1, AC2, AC3, AC4, AC5, AC7, AC8, AC9/A-B, AC9/A-E, AC11, AC14, AC12-16. The inorganic line had been producing, by different processes, ammonia both on gas and liquid phase.

Other materials obtained were: sodium carbonate, nitric acid, sodium nitrate and idrammina ammonia. Departments assigned to this line where: AM1, AM4, AM5, AM6. AM8, AM10 departments had been producing sodium and potassium cyanide; being the same process and equipment for the two products, were both obtained in the same plant. The framework of the process was based on: evaporation of Cyanide acid, reaction and crystallization of Cyanide‘s solution, filtration of Cyanide‘s crystals and final drying. Isocyanate as carbon oxide was produced in the TD2 department by using the poor gas that was fed from the AC1 department. CO and CO_2 were obtained by the adsorption on an ammonia-enriched solution; further treatments of adsorption and cooling permit to store pure CO. In parallel whit the adsorption reactions, H_2 gas was produced and sent to the assigned department.

Fig. 4.3.1 __Planimetria ubicazioni indagini‘‘ particular. 🟦 AM8 🟪 old buildings 🟩 Chlorine line 🟨 Acetate line 🟥 inorganic line**.** Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

4.4 Environmental characterization

As prescribed by the Master Plan, the characterization of the area had been performed by the use of a 50x50 m grid. More precisely, the Master Plan prescribe to individuate a sampling point over an area of 2,500 m^2 giving the possibility to choose the position of that point to the competent authorities. The use of such grid overcomes two issues that had been found in the area:

- the past used 100x100 m grid, prescribed by *Accordo per la Chimica*, was a too large approximation on a such heterogeneous area;
- the possibility of different location of sampling points rather than the vertices of the grid allows to overcome the presence of possible obstacles.

At the same time the use of the sampling grid allowed to set up a series of Thiessen polygon representing the averaged area under the influence of its own sampling point.

4.4.1 Sampling points

Going into details, in addition to the ancient sampling points, during the characterization of 2004 (performed by Syndial), 158 new sampling points had been added. 19 of the new sampling points were located into specific buildings, while 138 sampling point were distributed among the whole area. Each sampling point had been identified by the VP_number definition. The location of the sampling points could be seen in figure 4.3.1. Concerning the executive modalities of sampling point‘s perforation, it should be underlined that they had been all obtained by continuous-dry drilling technique; at the same time, it‘s necessary to make a distinction in function of the different aims of each sampling point modality:

- 117 sampling point (100 mm $Ø_{int}$, 127 mm $Ø_{ext}$) pushed down to 5.5 m and 10.5 m of depth from the top soil quote. Samples were analyze to assess the soil‘s chemical and physical status;
- 27 sampling points (100 mm $Ø_{int}$, 152 mm $Ø_{ext}$) pushed down to 5.5÷9.3 m from the top soil quote, equipped with piezometers to catch saturation water of the backfill soil;
- 14 sampling points (101÷130 mm $Ø_{int}$, 152÷177 mm $Ø_{ext}$) pushed down to 15÷17.5 m from the top soil quote, equipped with piezometers to catch primary aquifer‘s water.

4.4.2 Soil sample analysis

Physical analysis performed on soil samples, which results has been previously described, comprehends permeability tests (5 in situ, 5 lab test) and a series of geotechnical lab tests on cohesive samples. Chemical analysis were performed on 1,286 soil's samples (considered to be representative, where possible, down to 1 m depth) and at the same time on 161 top soil's sample (considered to be the first 20 cm down from the ground level or immediately under a concrete sole). Following the D.M. n. 471/99, on the 1,286 soil samples were assessed the following base parameters:

- pH;
- Dry residue at 105° C;
- Soil texture;
- Organic carbon;
- Ammonia;
- Free Cyanides;
- Total Cyanides;
- Fluorides;
- Metals: Al, Sb, As, Be, Cd, Co, Cr tot., Cr VI, Fe, Mn, Hg, Ni, Pb, Cu, Se, Sn, Ti, Tl, V, Zn;
- Aromatic solvents: Benzene, Toluene, Etilbenzene, Xileni, Stirene e Cumene;
- PAH: Naftalene, Acenaftilene, Acenaftene, Fluorene, Fenantrene, Antracene, Fluorantene, Pirene, Crisene, Benzo(a)pirene, Dibenzo(a,e)pirene, Benzo(a)antracene, Benzo(b,k,j)fluoranteni, Indeno(1,2,3-c,d)pirene, Dibenzo(a,h)antracene, Benzo(g,h,i)perilene; Dibenzo(a,l)pirene; Dibenzo(a,i)pirene; Dibenzo(a,h)pirene
- Carcinoghenic chlorinated aliphatics: Clorometano, Diclorometano, Triclorometano, Cloruro di vinile, 1,2-Dicloroetano, 1,1-Dicloroetilene, 1,2-Dicloropropano, 1,1,2-Tricloroetano, Tricloroetilene, 1,2,3-Tricloropropano, 1,1,2,2-Tetracloroetano, Tetracloroetilene, Tetraclorometano, 1,1,1,2-Tetracloroetano, Pentacloroetano, Esacloroetano, Esaclorobutadiene, Esaclorobutano, 1,3-cis-Dicloropropene, 1,3-trans-Dicloropropene, 1-Clorobutano,;
- Non carcinoghenic chlorinated aliphatics: 1,1-Dicloroetano, 1,2-cis-Dicloroetilene, 1,2-trans-Dicloroetilene, 1,1,1-Tricloroetano;
- Carcinoghenic alogenated aliphatics: Tribomometano, 1,2-Dibromoetano, Dibromoclorometano, Bromodiclorometano, Bromometano, Diclorodifluorometano (Freon 12), Triclorofluorometano (Freon 13);
- Nitrobenzenes: Nitrobenzene, 1,2-Dinitrobenzene, 1,3-Dinitrobenzene, 2-Cloronitrobenzene, 4-Cloronitrobenzene;

- Chlorobenzenes: Clorobenzene, 1,2-Diclorobenzene, 1,4-Diclorobenzene, 1,2,4-Triclorobenzene, 1,2,4,5-Tetraclorobenzene, Pentaclorobenzene, Esaclorobenzene;
- Non chlorinated phenols: Metilfenolo (o, m, p), Fenolo;
- Chlorinated phenols: 2-Clorofenolo, 2,4-Diclorofenolo, 2,4,6-Triclorofenolo, Pentaclorofenolo;
- Aromatic ammines: Anilina, 2-Anisidina, 3-Anisidina, 4-Anisidina, Difenilammina, 4-Toluidina, 2-Toluidina, 2,4-Diamminotoluene, 2,6-Diamminotoluene;
- hydrocarbons <C12;
- hydrocarbons>C12;
- Ftalates: Bis(2-etilesil)ftalato, Butilbenzilftalato, Di-n-Butilftalato, Dietilftalato, Dimetilftalato;
- PCB e PCT;
- Dioxins and furans.

On the contrary, on top soil sample were assessed parameters like dry residue at 105 ^{o}C, soil texture (> 2 mm), Asbestos by X ray diffraction method (XRD), Dioxins and furans (on 87 samples), PCB and PCT (on the same samples of dioxin tests).

4.4.3 Water sample analysis

Water analysis were performed on 41 new sampling points (27 of backfill saturation water and 14 of the aquifer) and on 44 ancient piezometer (17 of backfill saturation water and 27 of the aquifer). In addition to in situ analysis of pH, electric conducibility, DO, redox potential and temperature; following the D.M. n. 471/99 line and the Agreement program for chemistry, the parameters reported below were assessed during the characterization of the area.

- pH;
- Electric conducibilty 20°C;
- Redox potential;
- Dissolved Oxigen;
- Temperature;
- COD;
- Ammonia;
- Nitrites;
- Nitrates;
- Free Cyanides;
- Total Cyanides;
- Chorides;

- Fluorides;
- Sulphates;
- Metals: Al, Sb, As, Be, Cd, Co, Cr tot., Cr VI, Fe, Mn, Hg, Ni, Pb, Cu, Se, Ti, Tl, V, Zn;
- Aromatic solvents: Benzene, Toluene, Etilbenzene, Xileni, Stirene e Cumene;
- PAH: Naftalene, Acenaftilene, Acenaftene, Fluorene, Fenantrene, Antracene, Fluorantene, Pirene, Crisene, Benzo(a)pirene, Dibenzo(a,e)pirene, Benzo(a)antracene, Benzo(b,k,j)fluoranteni, Indeno(1,2,3-c,d)pirene, Dibenzo(a,h)antracene, Benzo(g,h,i)perilene; Dibenzo(a,l)pirene; Dibenzo(a,i)pirene; Dibenzo(a,h)pirene
- Carcinoghenic chlorinated aliphatics: Clorometano, Diclorometano, Triclorometano, Cloruro di vinile, 1,2-Dicloroetano, 1,1-Dicloroetilene, 1,2-Dicloropropano, 1,1,2-Tricloroetano, Tricloroetilene, 1,2,3-Tricloropropano, 1,1,2,2-Tetracloroetano, Tetracloroetilene, Tetraclorometano, 1,1,1,2-Tetracloroetano, Pentacloroetano, Esacloroetano, Esaclorobutadiene, Esaclorobutano, 1,3-cis-Dicloropropene, 1,3-trans-Dicloropropene, 1-Clorobutano,;
- Non carcinoghenic chlorinated aliphatics: 1,1-Dicloroetano, 1,2-cis-Dicloroetilene, 1,2-trans-Dicloroetilene, 1,1,1-Tricloroetano;
- Carcinoghenic alogenated aliphatics: Tribomometano, 1,2-Dibromoetano, Dibromoclorometano, Bromodiclorometano, Bromometano, Diclorodifluorometano (Freon 12), Triclorofluorometano (Freon 13);
- Nitrobenzenes: Nitrobenzene, 1,2-Dinitrobenzene, 1,3-Dinitrobenzene, 2-Cloronitrobenzene, 4-Cloronitrobenzene;
- Chlorobenzenes: Clorobenzene, 1,2-Diclorobenzene, 1,4-Diclorobenzene, 1,2,4-Triclorobenzene, 1,2,4,5-Tetraclorobenzene, Pentaclorobenzene, Esaclorobenzene;
- Non chlorinated phenols: Metilfenolo (o, m, p), Fenolo;
- Chlorinated phenols: 2-Clorofenolo, 2,4-Diclorofenolo, 2,4,6-Triclorofenolo, Pentaclorofenolo;
- Aromatic ammines: Anilina, 2-Anisidina, 3-Anisidina, 4-Anisidina, Difenilammina, 4-Toluidina, 2-Toluidina, 2,4-Diamminotoluene, 2,6-Diamminotoluene;
- PCB e PCT;
- Hydrocarbons (expressed as n-exhane);
- Linear chain petroleum hydrocarbons;
- Para-ftalic acid.

4.4.4 Soil status results

In line with the above mentioned aims of the thesis study, just results concerning Mercury and chlorinated compounds will be discussed.
Referring to D.M. n. 471/99 limits concentrations had been compared to the results obtained by the analysis on fine particulate soil (particles < 2 mm); briefly, exceeding of CLA were assessed on:

- metals such as Mercury, Arsenic. Of less abundance lead, copper, chromium and selenium;
- aliphatic chlorinated compounds such as vinyl chloride, di-tri-tetrachloroethylene, di-tri-tetrachloroethane;
- hydrocarbons both C > 12 and C < 12;
- PAH;
- aromatics such as ethylbenzene, xylene, styrene, cumene;
- PCB;
- Dioxins and furans
- Phathalates.

4.4.4.1 Mercury

From the comparison between figure 4.3.1 and figure 4.4.4.1 is possible to relate the actual contamination to ancient productive sectors. In particular, Mercury values over the CLA (5 mg/kg D.M. n 471/99 industrial soil) were found both on ex-productive site and areas that were not assigned to any facility. Anyhow, it should be underlined that, considering all the sampling points, Mercury contamination is limited to the backfill soil; in most of the cases at 2-2.5 m depth, concentrations were found to exceed the limits of few mg. Sampling points attributable to productive areas had shown concentrations in ranges of 95 mg/kg, 156 mg/kg respectively for 1-1.5 m and 1.5-2 m depth in the nearby of CS3 department; extraordinary concentration of 1,300 mg/kg was found in the nearby of Lusore canal in the between of CS1 and TR3 departments. Furthermore, close to CV10 plant, were found concentrations higher than 10 times the CLA limits. It seems to be reasonable to attribute this concentrated contamination points to spills or accidents in Mercury-solutions management or Mercury catalyser and cathodes storing. On the other side, it seems to be rational to relate the contamination of hot spots far from CS or CV production plants to the common used practice of backfilling. In particular, considerable concentrations were found in the proximity of the Lusore canal in two sampling points that presents almost the same concentrations in ranges of 250 mg/kg on the first meter of depth.

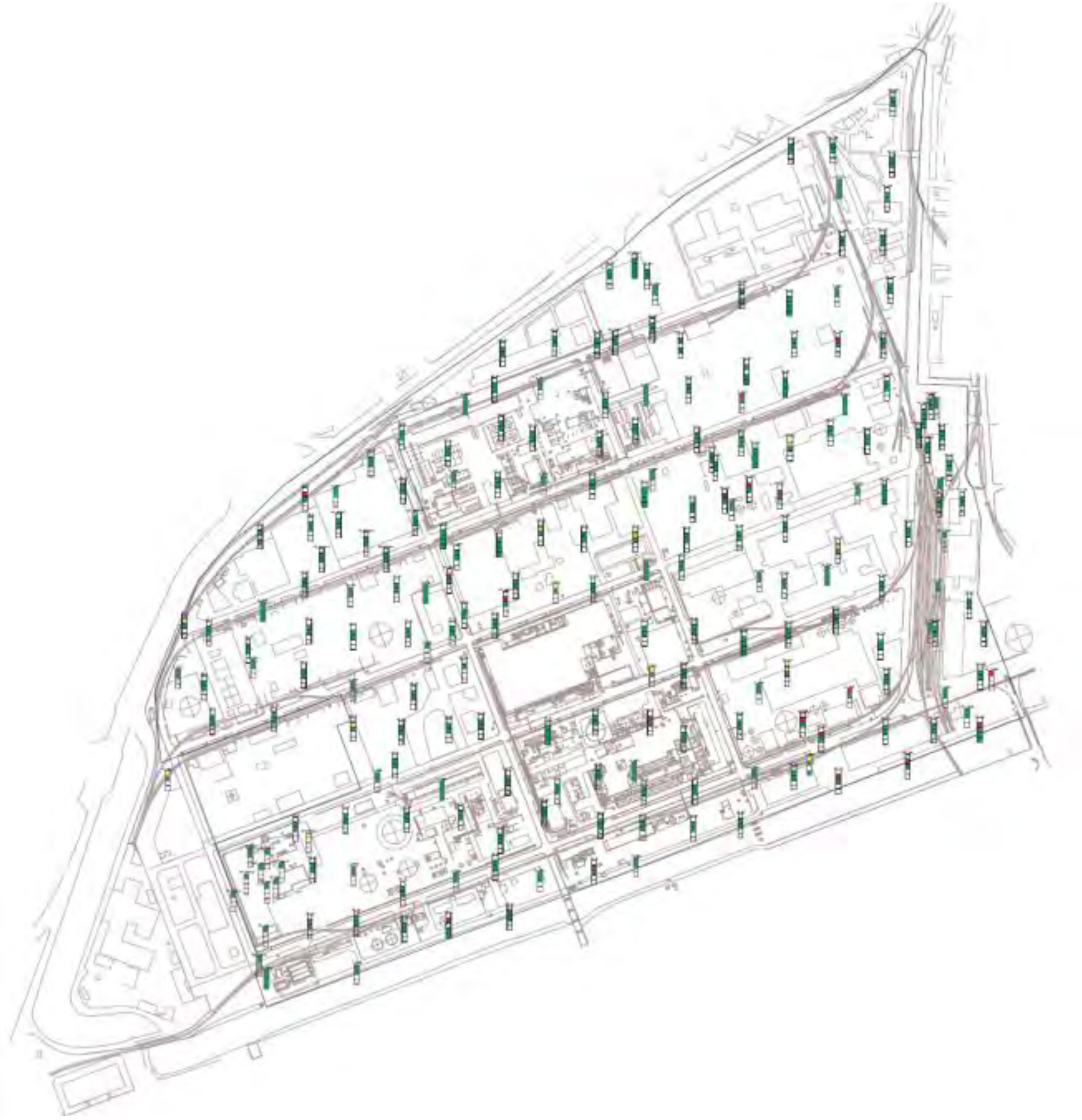


Fig. 4.4.4.1 _Distribuzione della contaminazione nei terreni; Mercurio‘‘ particular. Concentrations 🟩 < CLA, 🟨 CLA-2CLA, 🟥 2CLA-10CLA, 🟪 >10CLA. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

4.4.4.2 Chlorinated compounds

Concerning chlorinated compounds pollution in soil, the relationship between productive departments and source of contamination is evident. As could be seen in figure 4.4.4.2, the whole area assigned to VCM and PVC production is almost uniformly polluted, peaks on concentrations were found in the proximity of CV1,CV10,CV11 and CV14,CV15, CV16.
Focusing on VCM contamination, once it has been reminded that the reference law‘s limit is 0.1 mg/kg, almost 40 sampling points had shown concentrations higher than 2-10 times or even higher 10 times the CLA. Furthermore, it is worthy to be underlined that VCM contamination did not affect just the backfill soil as considerable concentrations were found on first impermeable layer and aquifer as well, pollution had demonstrated to be present also in secondary impermeable layer just in 4 sampling points. In terms of concentrations, related to production source, most significative results had shown:

- in the nearby of CV10, CV11 plants ranges from a minimum of 0.19 mg/kg to a peak of 6.7 mg/kg affecting the first impermeable layer at 9.5-10.3 m depth. Concentrations over than 2-10 times CLA were found down to the secondary impermeable layer;

- in the nearby of CV1 plant ranges from a minimum of 0.19 mg/kg to a peak of 23 mg/kg affecting the backfill soil at 3-3.8 m depth;

- close to CV14,CV15, CV16 departments peak concentration of 66 mg/kg was found on backfill soil at 1.4-1.9 m depth.

At the same time, concerning isolated sampling points that seems not to be related to any production department, remarkable concentrations were found along the Lusore canal, in the nearby of AM8 department and in a part of the acetate‘s line affecting backfill soil and primary impermeable layer.

Fig. 4.4.4.2 _Distribuzione della contaminazione nei terreni; VCM‘‘ particular. Concentrations 🟩 < CLA, 🟨 CLA-2CLA, 🟥 2CLA-10CLA, 🟪 >10CLA. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

4.4.4.3 Other pollutants

Briefly, among the results concerning other pollutants, it should be given particular stress on the diffused presence of Arsenic in the area between AC2 and CV14-16; the diffused presence of organic-chlorinated compounds even down to the secondary impermeable layer, affecting with considerable concentrations the CV, TR and TS area. Lumped hotspots of PCB contamination, affecting randomly top soil or backfill soil, were found along Lusore canal, close to the VC line and in the nearby of electric cabins. Dioxins and furans were punctually found close to the thermal power plant and electric cabins respectively affecting top soil and even backfill soil.

4.4.5 Water status results

Concerning water results it should be reminded that samples, as done for soil distribution assessment, were taken for saturation water of the backfill soil and aquifer as well. A brief summary of the results of the most concerning pollutants will be given in addition to a focus on VCM and chlorinated compounds pollution.

4.4.5.1 Saturation water of backfill soil

Results taken from 44 piezometers among the area, in a two months period of observation in winter, had shown great limit‘s exceeding related to the following pollutants:

- Metals as Arsenic, Iron, Manganese and Aluminium ; less relevance traces of Lead, Nickel, Selenium and Vanadium were found;
- aliphatic chlorinated compounds such as Vinyl Chloride, di-tri-tetraChloroethylene, di-tri-tetraChloroethane;
- aromatic compounds such as Benzene and Toluene;
- total hydrocarbons;
- PAH;
- PCB;
- Dioxins and Furans.

4.4.5.2 Chlorinated compounds

Results concerning chlorinated compounds contamination reveal a different and more dramatic scenario in comparison to the above mentioned pollutants: almost the entire sets of samples was found to be above the law limits for each of the chlorinated compounds searched.

As it could be guessed from figure 4.4.5.2; VCM was found to be widely present over the area (almost the 70% of the whole samples), reaching the most considerable concentrations in piezometers in the nearby of VCM and PVC departments. Sampling points VP_91, N_2863 in proximity to CV10, CV11, CV 16, CV14 and TS1-2 shows concentrations even 100 times higher than the CLA level (0.5 µg/l), reaching the maximum concentration at 15,200 µg/l. Same order of magnitude of concentrations were found in the nearby of CS5, CV3 and AC1 departments. Looking at the above mentioned results on soil samples and knowing the great mobility of VCM on soil, it could be reasonably deduced that this compound was able to move from the soil matrix down to the saturated media in great quantity due to the superficial water table fluctuations.

In parallel, tetraChloroethane. Concentrations above the CLA limits were found to be homogenously distributed among the area with the exception of two sampling points. Orders of magnitude are in the ranges of 10 to 100 time higher the CLA in the majority of the samples, while levels 100 times higher (up the maximum value of 8,000 µg/l) were found to be distributed in the downstream VCM and PVC plants and in the nearby of the Lusore canal.

Likewise, diChloroethane and triChloroethane were found to be diffusely present but with a more heterogeneous distribution; peaks of concentrations were asses on the VCM area with 700µg/l and 740µg/l respectively. Chlorinated solvents such as 1,2-cis-dichloroethylene was found to be punctually spread over the area, showing concentrations in ranges of 10 to100 times the CLA in proximity of VCM departments and Lusore canal; peak of concentration was found in N_2683 with 73,000 µg/l. In parallel, 1,1-dichloroethylene was found to be more widely distributed along Lusore canal and among CV, CS and acetates departments with concentrations higher than 100 times CLA limits.Furthermore, other chlorinated solvents such as trichloroethylene and tetraChloroethylene were found to be present in almost the sampling points. More precisely, triChloroethylene was found in all the sampling points (with the exception of two piezometers) to be present in concentrations higher than two orders of magnitude than the CLA (1.5 µg/l); peak concentration of 90,000 µg/l was asses closed to TR4 and CS3 departments. Similar distribution was found for tetraChloroethylene with maximum concentration of 20,000µg/l.

Fig. 4.4.5.2 __Distribuzione della contaminazione nelle acque di impregnazione del riporto; VCM‘‘ particular. Concentrations 🟢 < CLA, 🔴 CLA-2CLA, 🟣 2CLA-10CLA, ⚫ >10CLA. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

4.4.5.3 Other pollutants

Iron and Manganese were found to be heterogeneously distributed among the whole area; more precisely, their concentrations were found to be above law limits on 60 % and 80 % respectively of water samples. Even if peaks of Iron concentrations were found in the nearby of chlorine line departments and storage tanks, the correlation between water and soil concentrations is not ensured. In fact, as any speciation of Iron on soils was prescribed by law, any information about Iron distribution is present; however, even if iron may naturally occur in soils at high concentrations and the distribution of concentration interest such a wide area, it seems to be reasonable to consider the iron water concentration as a consequence of soil contamination. It has to be reminded that almost the whole area was backfilled with dredging sediments and processing wastes; at the same time temporary storage, accidents and spills were not infrequently among the area. Not surprisingly, peaks on iron concentrations were found in the nearby of VCM line departments that had been using iron catalysers during its processes or had been storing wastewaters and other products. At the same time, Arsenic was found on a considerable number of sampling point (50% of the whole samples) in concentrations above law limits; in this case, by the data given on soil characterization, in exception of few sampling point, peaks on water contaminations corresponds just to traces on soils. Punctual concentrations of Aluminum , Lead, Nickel and Vanadium above law limits were found. Concerning organic pollutants it should be underlined the presence of Benzene (50% of the whole samples) in the nearby of acetic and inorganics departments; few samples were found to overcome law limits for Toluene and Xylene. Total hydrocarbons (expressed as n-hexane) were found to be above law limits (350 µg/l) in just two sampling points but characterized by considerable concentrations of 480 µg/l and 27,000 µg/l respectively. PCB‘s exceeding concentrations were found on just two sampling points. Dioxins were found to be over CLA on just one sample; its concentration (73.5×10^{-6} µg/l) was asses to be more than 10 times higher than law limits concentration (4×10^{-6} µg/l).

4.4.6 First aquifer

Results referred to 41 sampling points among the area on the same observation period of saturation water samples. A general scenario of the contamination status could be summarized as follow.

4.4.6.1 Chlorinated compounds

Similarly to the saturation water of the backfill soil, the aquifer had manifest a severe contamination by chlorinated compounds diffused on the whole area. More precisely, as it could be guessed from figure 4.4.6.1, VCM was present in almost the totality of sampling points with the majority of concentrations in ranges from 10 to 100 times CLA or even higher than 100 times. Even in this case the distribution of concentration had affected with the maximum values the area assigned to chlorine departments; peaks of 115,000 µg/l and 61,300 µg/l were found in the nearby of CV 14 and AC7 plants. 1,2-dichloroehtane, trichloroethane and tetrachloroethane were found to be present in almost the whole samples analyzed; with the exception of two sampling points, 1,2-dichloroetane ranged from CLA values to concentration up to 660,000 µg/l among the area. In parallel, trichloroethane, that was present in almost the 78% of the samples, reached peak concentration at 31,500 µg/l; similarly, tetrachloroethane had reached maximum concentration at 73,000 µg/l among the 85% samples contaminated. Likewise, from 1,1-dichloroethylene distribution it could be stated that the majority of the sampling points, among the 85 % of the whole set of polluted samples, are characterized by concentrations over 100 times CLA values. Peak value of 29,000 µg/l was found in the nearby of the AC 7 department. At the same time, 1,2-cis-dichloroethylene is present, with concentrations above the CLA, on the 76% of the analyzed samples; maximum concentration (150,000 µg/l) was found close to CS3 department. Trichloroethylene was found in each sampling point among the area with the majority of concentrations above 100 times the CLA value. Maximum values were asses on the eastern part of the area reaching concentrations like 600,000 µg/l (CS3 plant), 103,000 µg/l (CV10). In parallel tetrachloroethylene was found to be present, with the exception of two sampling points, in all the samples. Peak concentration of 17,500 µg/l was found in the proximity of CS3 plant. Other chlorinated compound such as di-tri-tetrachloromethane, chlorobenzene and di-trichloropropanes were punctually found among the area.

Fig. 4.4.6.1 _Distribuzione della contaminazione nelle abcque di prima falda; VCM'' particular. Concentrations 🟢 < CLA, 🔴 CLA-2CLA, 🟣 2CLA-10CLA, ⚫ >10CLA. Source: Risultati caratterizzazione integrativa (Set. 2005) Syndial.

4.4.6.2 Other pollutants

Metal's presence above CLA limits was found in almost all the examined samples; in particular it should be mentioned the presence of Iron, Manganese and Arsenic in 88 %, 80 % and 80,5% of the total samples respectively. This contaminant, Iron and Manganese, were associated to homogeneous distribution among the area showing peak concentrations at 32 µg/l (iron) and 7,500 µg/l. On the contrary, Arsenic distribution seems to be more localized in the eastern part of the area. Comparing the averaged distribution of concentrations on saturation water and aquifer, Iron and Arsenic seems to be present with higher concentrations in the aquifer. Other metals such as Nickel and Aluminum were found in few sampling points, with maximum concentrations of 68 µg/l and 3.21 µg/l respectively. Benzene was found to be present in almost the 80 % of the water samples, most of the contaminated piezometers shows concentrations up to 10 times the CLA values (1 µg/l); hotspots with concentrations over 100 times the law limit were present in the eastern part of the area (VCM, CS and PVC departments). The presence of other aromatic compounds, in particular Toluene above law limits, was manifested on just seven samples; simultaneously in the same samples was found benzene. Total hydrocarbons, analyzed as n-exhane, were found to be over the law limit (350 µg/l) in the same area of aromatic compounds pollution; in the nearby of CS3 and CV1 departments concentrations of 68,000 µg/l and 18,000 µg/l were respectively found. Lumped hotspots of PCBs contamination were found among the area in the nearby of Lusore canal (0.1 µg/l), in proximity of CV8 department (0.2 µg/l) and in other two isolated sampling points (0.03 µg/l and 0.1 µg/l). In parallel, two significative hotspots were found to be affected by Dioxins concentrations above the law limit (4 pg/l); concentrations of 13.51 pg/l and 9.47 pg/l was respectively found in the nearby of chlorine productive departments and on the western part of the area.

4.4.7 ARPAV cross-examination

Simultaneously to Syndial characterization of the area, ARPAV had performed the cross-examination required for data validation. As prescribed by the Agreement program, 10% of the entire set of samples (149 samples divided between top soil, soil and groundwater) had been collected during 23 days of sampling campaign. As it could be easily guessed, in order to be comparable, samples must be analyzed with the same method by ARPAV and private laboratories; in parallel, samples have to be collected by chance within the area. It should be underlined that the aim of ARPAV's validation is to assess whether the whole data set is sufficiently representative of the contamination thanks to a statistical procedure based on the comparison between sample and cross-samples. More precisely, by following the old validation procedure, evaluation of the quality of data was driven by two requirements:

- Variation between ARPAV and private data (considering each data) could not be accepted if it is greater than ± 50% for inorganic parameters and ± 100% for organic parameters;
- Data affected by non-acceptable variation could represent at maximum the 30% of the whole data set.

It should be pointed out that nowadays the validation method had been sophisticated to a more sensitive procedure. More precisely, the current process works as a linear regression between samples and cross-samples in order to evaluate the systematic overestimation or underestimation of the values; ARPAV cross-sample‘s values are arranged into x axis while company sample‘s values are disposed into y axis. Each couple of value (sample and cross-sample) is identified by a coordinate into the x-y plane; consequently, a linear regression interpolation is used among the whole data. The comparison between the slope of the calculated line and the bisector line evaluates the trend of the difference among samples and cross-samples; in case of a systematic underestimation of the value over the whole data set (considered to be the 10% of the entire set of samples), the 90% of data are considered to be equal to: $y^* = \frac{y-a}{b}$; where y is the old value, a and b features of the regression line. It should be pointed out that this kind of validation method is suitable in case of systematic errors rather than lumped errors; in parallel, a great limitation of the procedure is related to the assumption that ARPAV‘s values are considered to be not affected by errors during the laboratory assessment. However, concerning the characterization that had been presented in previous chapters, ARPAV‘s cross-examination had validated the whole samples presented by Syndial.

4.4.8 Environmental characterization conclusions

Summarizing the results obtained, it could be stated that:

- it could not be confirmed a relationship between metal presence in soil and consequently in water, but, on the other hand, it seems to be reasonable to relate metal‘s concentrations (Iron and Manganese) in the two water bodies;
- Aromatic compounds (in particular Benzene) were punctually present in soils, conversely, were diffusely present on the two water bodies;
- Organochlorinated compounds were asses to be diffusely present both on soil and water matix; rarely, pollutants found in soil match with the ones found in water of the same sampling point.

4.5 Remediation working progress in Porto Marghera

It‘s seems to be reasonable, after the characterization of the area, to report a brief introduction of the state of the art of the remediation plan in the contaminate site. Starting from this general description the focus will be then moved on the metal‘s remediation and the ECRT application.

As it had been previously described, Porto Marghera presents an highly heterogeneous contamination ranging from inorganic to persistent organic pollutants; furthermore, both soils and groundwater had been demonstrated to be affected by significant pollution. Consequently, as it could be easily guessed, different kind of remediation techniques had been engineered on the area. Concerning contaminated soils, almost the 54% of the total area had been characterized and planned by an approved remediation plan, on the contrary about 36% of the site had been not interested by remediation project so far; just on the 5% of the contaminated spots remediation are runnning. Dealing with contaminated groundwater, almost the 50% of the total area had been planned by an approved remediation plan while for the 39% of the site any project had been presented; about on the 12% of the contaminated spots remediation are running (Regione Veneto: Sezione Progetto Venezia,2014).

Fig. 4.5.1 Working progress of remediation; 🟫 Approved remediation, 🟪 Authorized landfill, ▨ Permanent securing measure 🟩 Certified soil‘s remediation project, 🟧 Activate remediation plan, 🟨 Remediation plan approved by decree, 🟥 Presented remediation plan. Source: Regione Veneto: sezione progetto Venezia

In order to give an idea of the several applications that are planned to be used among the area, in figures 8.2 and 8.3 are presented particulars of 2007 GIS application given by APAT:

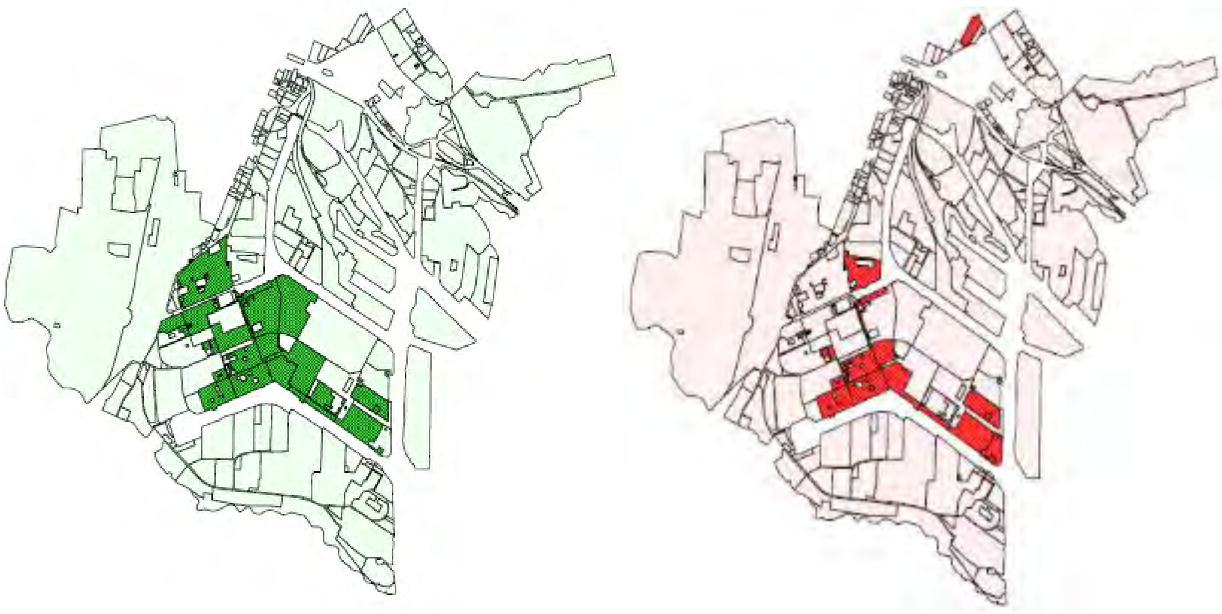


Fig. 4.5.2 🟩 areas planned for MPE/TPE treatment, 🟥 areas planned for SVE treatment. Source: D'Aprile, 2007.

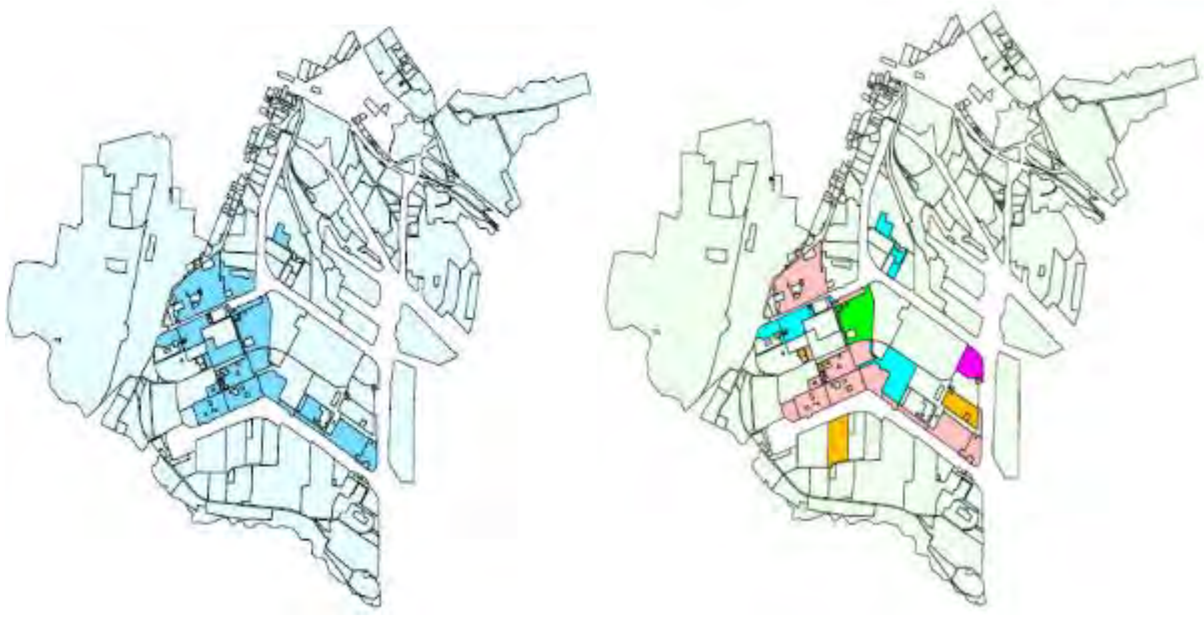


Fig. 4.5.3 ▨ areas planned for ISCO treatment, 🟧 areas planned for bioremediation treatment, 🟪 areas planned for aerobic degradation, ▭ areas planned for ECRT, 🟦 areas planned for MISP treatment, 🟩 areas planned for phytoremediation and MISP treatmen. Source: D'Aprile, 2007.

It should be pointed out that the timetable for treatments mostly ranges from 10 to 30 years of duration (D'Aprile, 2007).

5. REMEDIATION OF METAL'S CONTAMINATED SITES

Dealing with heavy metal pollution, in this paragraph an overview of the most suitable soil remediation techniques will be presented, particular stress will be given to ECRT. Sources of heavy metal pollution may be various, spacing from industrial plants as electroplating or Chlor-alkali to atmosphere deposition or natural phenomena related to rock‘s weathering (Wuana *et al.,* 2011). The relevance of metals contamination of both soil and water matrices is of great concern such that European committee had defined as priority pollutants Cadmium, Copper, Lead, Mercury, Nickel and Zinc. The hazard related to metal‘s contaminated sites had been evidenced by several scientific studies and epidemiologic research (Smith *et al.,* 1999). Furthermore, environmental consequences associated to heavy metals pollution are in function of several variables forcing the matrix or the metal‘s nature as well. It should be reminded that in order to be hazardous the metal or metalloid compounds must be able to reach a target (plants, animals, humans); in other words it could be stated that the risk associated to metal contaminated depends on its speciation and so to its bioavailability (Kumpiene *et al.,* 2010; Gadd *et al.,* 2009).

5.1 Environmental fate of metals

Metal‘s ions may be susceptible to different processes once reached the medium, in particular, fundamental dynamics of metals may be summarized as:

- *Sorption/desorption processes:* is based on the electrostatic attraction related to the unbalance of ions charges on soil and solution (Bolan *et al.,* 1999). It had been demonstrated that the dynamic of sorption and desorption is related to both soil and metal-solution properties (Bolan *et al.,* 2014); in particular, evident relations were asses for low ranges of pH and presence of organic matter. At the same time, biosorption of metals into microbial cells had been proved to be an effective pathway in soil matrix (Gadd *et al.,* 2009).

- *Precipitation/dissolution:* on the contrary of desorption process, precipitation is based on high range of pH; it had been demonstrated to be influenced by the presence of different liming material such as $CaCO_3$, $Ca(OH)_2$ and $CaSO_4$ (Hong *et al.,* 2007) and bacterial populations (Gadd *et al.,* 2009). Recently had been demonstrated the effective induced stabilization of metals in soils thanks to the presence of plant‘s roots (Jadia *et al.,* 2009).

- *Oxidation/reduction:* reactions of e^- exchange that may be induced by both chemical amendments and microbial cultivations; several natural oxidation or reduction pathways occurs in soils thus to induce changing in the metal status (Bolan *et al.,* 2014). It should be underlined that this kind of transformations greatly affects the mobility, the toxicity and the susceptibility to other processes of the metal itself (Gadd *et al.,* 2009).

- *Methylation/demethylation:* set of reactions, occurring both on soil and saturated media, that improve the volatilization behavior of the metal-metalloid compound by the addition of a methyl group. Even if abiotic methylation could take place, biological processes seem to be the dominant processes (Bolan *et al.,* 2014). It should be underlined that methylated compound could be even more toxic than their metalloids precursors (Rani *et al.,* 2011).

5.2 Remediation techniques for metal's contaminated sites

Concerning remediation techniques for metal contaminated soils, several study and full scale applications were performed both in-situ and ex-situ. As suggested by Yao *et al* in 2012, remediation options may be grouped into physical, chemical and biological families. It should be anticipated that in most of the cases the remediation of the site is obtained by the combination of different reactions occurring at the same time (Khan *et al.,* 2004).

5.2.1 Physical treatments

Commonly considered as highly invasive techniques, physical treatments are usually preferred to others thanks to its simplicity and velocity on soil remediation (Yao *et al.,* 2012). Varying from soil replacement to thermal desorption procedures, these kind of processes offer a wide set of applicability options. Briefly, the main physical treatments could be described as follow taking into consideration both advantages and drawbacks:

- *Soil replacement*: it works as a dilution of the pollution by excavation and renewal of the contaminated soil; if from one side it is a fast and effective treatment, from the other side it is limited to small and low grade contaminated sites due to the high cost of mining and replacing (Yao *et al.,* 2012). More importantly, it should be underlined the possibility of creating a secondary source of pollution once disposed the contaminated soil away from the site.

- *Mechanical separation*: based on grain size or magnetic sorting, this kind of processes are used both as pretreatments and beside treatments. Pollutants are removed by the soil matrix (ex situ) by removing the smaller (<10–20 μm) particles from the coarser fraction. These kind of methods are of particular concern due the high simplicity and cost effective features; moreover, it could be easily combined with other remediation techniques (Mulligan *et al.,* 2001).
- *Isolation and containment*: physical or hydraulic barriers may be used to contain and isolate the source of contamination without performing any reaction on the pollutants. Barriers made of steel, cement, clayey or synthetic material could be used for both

vertical barriers and horizontal capping; extraction wells could be used whenever the barrier could not reach the impermeable layer down in the polluted soil (Khan *et al.*, 2004).

- *Thermal desorption*: by using ranges of temperatures from almost 100 to 600 °C, thermal desorption spoils the volatility tendency of pollutants by the heating of the soil matrix with different conductors such as steam, microwaves or radiations. The simplicity of the process itself is limited by the use of sensible instruments and high energy demand; it should be underlined that, after the long period of treatment required, reuse of the remediated soil is possible (Wang *et al.*, 2012).

- *Vitrification*: similarly to thermal desorption, vitrification process consist into the heating of the contaminated soil in order to induce volatilization of pollutants; at the same time, due to the high temperature's ranges used (1400~2000 °C) melting of the soil matrix and volatilization of organic matter occur (Yao *et al.*, 2012). Its use is limited due to the high energy effort required to induce the melting of the soil and at the same time due to the impossibility of soil reuse after remediation and high costs.

5.2.2 Chemical treatments

Throughout the addition of chemical amendments several reactions, such as chelation, precipitation, adsorption or ion exchange, may be induced between soil matrix and liquid solution. The most effective chemical treatments on metal contaminated soils could be described as follow:

- *Soil flushing/Soil washing*: these two methods both deal with the injection of fresh water of solvents in order to induce the solubilization of metals into the leachate; while soil flushing acts in situ, soil washing is performed ex situ. Considering soil washing it should be underlined that the solubilization process is performed on reactors and the use of more aggressive solvents than water lead to shorter time for remediation; at the same time costs for excavation, pretreatment and post treatments of the soil and waste water management must be taken into consideration (Wuana *et al.*, 2011).
  On the other hand, costs of excavation and pretreatment are null for soil flushing processes; in this case it should be underlined the securing measures to be adopted to avoid groundwater pollution and at the same time the long time required for remediation due to the diffusion processes in soil. Great limitations of the flushing's processes are related to the soil conditions of pH, CEC, permeability and clay presence (Khan *et al.*, 2004). However, it had been demonstrated that both the techniques are effective on metal

remediation (Mulligan *et al.,* 2001; Khan *et al.,* 2004) and further recover of metals is possible.

- *Stabilization/Immobilization*: aim of immobilization is to reduce the bioavailability and the mobility of pollutants by reactions of adsorption, precipitation, and complexation forcing the solution and the solid phase. These reactions are enhanced by the use of several chemical compounds such as phospates, metal oxides, liming materials and even organic compost (Bolan *et al.,* 2014). It should be reminded that the effectiveness of the procedure greatly depends on the pollutant characteristics and on soil conditions; as reported by Mulligan in 2001, metals such as As, Cr, Hg are not suitable for immobilization due to their poor tendency to form insoluble hydroxides. In parallel, solidification techniques are often used on metal contaminated soils in order to reduce the mobility of the pollutant by chemical reactions of encapsulation and sealing of the whole soil matrix .(Khan *et al.,* 2004).

5.2.3 Biological treatments

Even if biological and biochemical remediation for metal contaminated sites are not fully developed yet (Mulligan *et al.,* 2001), a brief parenthesis should be opened about this kind of gentle and green remediation techniques.

- *Bioleaching, Biosorption, Bioxidation/Bioreduction*: it had been demonstrated that bacteria are able to force changing into oxidation's state thus to induce reactions such as leaching, precipitation, adsorption (Garbisu *et al.,* 2003; Yao *et al.,* 2012). More in details, as reported by Bosecker in 1997, bioleaching is the ability of specific kind of bacterial populations to turn heavy metals sulfides into water-soluble sulfates; these processes had been demonstrated to be dependent on several working conditions such as nutrients presence, biotic metal tolerance, pH; in parallel they could be considered as the combination of chemical and biological pathways (Bosecker *et al.,* 1997). Several different biosorbents may perform metal sorption both living and dead biomass (Volesky *et al.,* 1995). Several studies had proved the ability of bacteria to force oxidation and reduction reactions on metals (Rajendran *et al.,* 2003; Garbisu *et al.,* 2003 ; Ahalya *et al.,* 2003, Yao *et al.,* 2012) thus to change its mobility and toxicity. By literature's review it should be underlined that further studies should be performed; however, it could be stated that bioremediation processes may be suitable for low grade contaminated soils and long-time periods but low expensive costs are expected (Mulligan *et al.,* 2001).

- *Phytoremediation*: plant's ability of metal remediation is known since the early years of the 19th century and several studies and few full scale applications had been performed yet. The phytoremediation process involves a series of different biotic and abiotic reactions simultaneously occurring in the nearby of the roots (rhizosphere) in combination with the soil‘s microbes (Yang *et al.,* 2005). As reported by Pulford in 2002, fundamental steps of phytoremediation process may be individuated into phytoexctraction, phytodegradation, rhizofiltration, phytostabilization and phytovolatilization. Among these reactions, particular effectiveness on heavy metals remediation had been demonstrated for phytoextraction and phytostabilization (Ali *et al.,* 2013). As reported by Garbisu in 2001, plants used for phytoextraction had shown the tendency to accumulate in its bodies (roots and shoots) both metals required for metabolic processes (Fe, Mn, Zn, Cu, Mg) and heavy metals that were not required for plant‘s development (Cd, Cr, Pb, Co, Hg, Ag, Se). Most probable pathways of phytoextraction consist into metal-mobilization by root‘s exudates, absorption or adsorption and final chelation of the metal into the plant‘s body (Ali *et al.,* 2013; Yang *et al.,* 2005). In parallel, phytostabilization processes had been proved to be effective on the reduction in mobility and bioavailability of metals thanks to the roots excretions of redox enzymes. Different reactions, such as precipitation, complexation and chelataion, concur to the phytostabilization process (Ali *et al.,* 2013). It should be underlined that phytoremediaton is particularly interesting technique thanks to its low capital costs, poor invasion on the site and possible recover of materials ; at the same time great limitations still affects time required for remediation, size of roots and shoot of hyper accumulator plants and development into highly contaminated soil. However, recent research are testing the use of bioengineered plants and the combination of plants and chemical amendments.

As it had been previously discussed, the remediation of a contaminated site is often related to the combination and the synergy of different processes and reactions; improvements of these features were tested and then commonly used as remediation techniques. Examples of mixed treatments may be phytoremediation practices in combination with the addition of chemicals (Wuana *et al.,* 2011), chemically enhanced bioremediation (Garbisu *et al.,* 2003), biological enhanced immobilization techniques.

PART 2: MATERIALS AND METHODS

6. ECRT

Still nowadays, electrochemical remediation techniques is considered to be an emerging technology for soil and groundwater contamination; it has to be underlined that, even if effects of electric fields on soil matrices are tested and modeled since the early years of the 18th century, electrochemical techniques became interesting for soil remediation just on the late 1980's (Morales *et al.,* 2002). More precisely, at first, technologies using direct current (DCT-EKRT Electro Kinetic Remediation Techniques) had been used for geotechnical purposes of stabilization and drying of soils; later on, as soon as evident traces of inorganic and polar compounds were found into wastewater of EK treatments, more interest was given to EKRT as a contaminated soil remediation use (Ferrarese *et al.,* 2008). Through the years, ECRT had been proved to be effective on both organic and inorganic pollutants affecting saturated and unsaturated matrices as well; the flexibility as in situ and ex situ remediation, the low impact on landscape and environment, the effectiveness on fine grained soils and the quite contained costs made ECRT a promising remediation solution (Virkutyte *et al.,* 2002; Mulligan *et al.,* 2001; Niroumand *et al.,* 2012). It should be reminded that following chapters have to be handled just as a general overview on ECRT; further details concerning geological or chemical concepts are beyond the scope of this text.

6.1 ECRT fundamentals

Fundamentals of ECRT may be resumed into the combination of a series of physical transport pathways and electrochemical redox reactions induced by the forcing of a direct current passing through the soil between two electrodes. Had been demonstrated that the whole set of processes made possible metal's mobilization and organic's degradation (Maini *et al.,* 2000; Ferrarese *et al.,* 2008; Negrete *et al.,* 2013). In order to give a clear and synthetic overview of the ECRT mechanism, it could be stated that the soil-water domain works as an electrochemical cell where the current flow induces reactions of oxidation and reduction respectively at the anode and cathode. More precisely, among the soil matrix, each soil particle behaves like a capacitor able to accumulate and release the converted electric energy several times per second (Rahner *et al.,* 2002). This means that each of the soil particle, once had been polarized, acts as a microelectrode system thus inducing redox reactions among the whole soil's domain and not just in the nearby of the two electrodes on the soil. The above mentioned concepts of induced polarization and capacitor behavior are strictly related to soil's nature, structure and characteristics; concerning clayey mineral, as it had been reported by several authors, the negative charge distributed over the clay surface is a consequence of the natural formation of the mineral itself. The presence of this negative charge attracts positive cations close to the mineral boundaries thus creating the so called double diffused layer. It should be underlined that due to the presence of the double diffused layer a voltage difference is present in the nearby of the clay particle (Acar *et al.,* 1995). Many models of this structure had been proposed through the years

(Helmotz, Gouy-Chapman, Stern); anyhow, to simplify and do not go into further details, it could be considered to be sufficient the sketch in figure 6.1.1 to fix the concept:

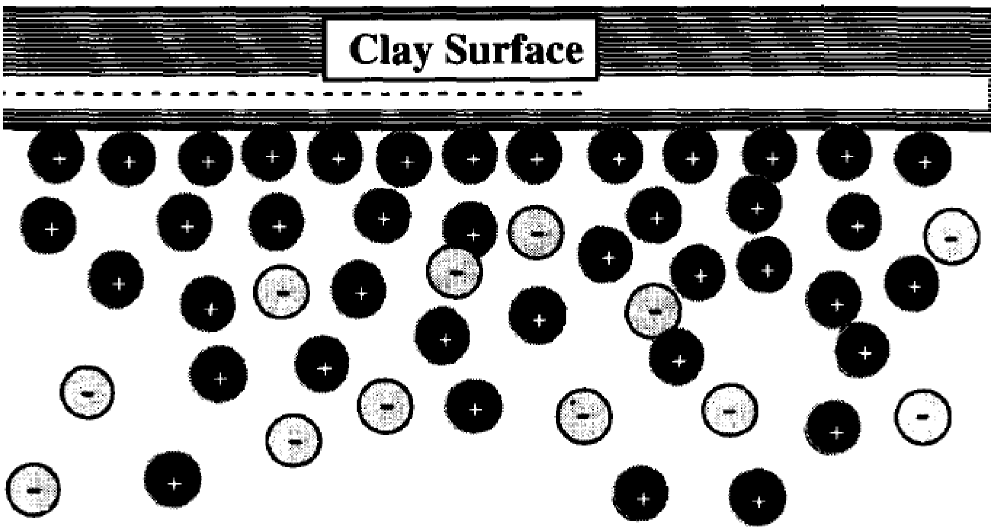


Fig. 6.1.1 Particular of charge distribution close to clayey particle. Source: Acar *et al., 1*995.

6.2 ECRT mechanism

As it has been previously mentioned, ECRT works as a synergy of different physical and chemical reactions; in particular, as presented by different authors (Virkutyte *et al.,* 2002; Acar *et al.,* 1995; Morales *et al.,* 2002) , it should be stressed out the role of the following pathways of transport:

- Electroosmosis.
- Electromigration.
- Electrophoresis.

6.2.1 Electroosmosis

Electroosmosis could be considered as the movement of the pore water, or any other liquid, from the anode to the cathode among the soil matrix (Virkutyte *et al.,* 2002), at the same time, through the motion of water both organic and inorganic species will be transported. As reported by Page et al (2002), the dynamic of the electroosmotic flow (q_A) could be compared to an hydraulic flow driven by Darcy's law like:

$$q_A = -k_e E A$$

where k_e is a coefficient of electroosmotic conductivity, E is the electrical field strength and A is the cross sectional area normal to flow's direction. Further and more sophisticated model has been introduced taking into consideration medium and liquid characteristics (Page *et al.*, 2002); however, it could be stated that electroosmotic flow depends on both the electrical field forces and the dissipative forces between the soil and the water (Helmholtz-Smoluchowski model). It is widely accepted to relate elecroosmotic transport to the presence of the double diffused layer. More precisely, the induced electric field forces counter ions on the double diffused layer to electrodes thus causing a shear stress in the hydratation shell of the soil particle; consequently the shear stress in soil particle proximity is converted into a shear force able to move pore water (Morales *et al.*, 2002). Evidences had proved that the electroosmotic flow moves mostly from the anode to the cathode direction reasonably due to the abundance of cations in the double diffused layer (Acar *et al.,* 1995). Figure 6.2.1.1 presents a graphic summary of the electroosmotic pathways stressing out the presence of double diffused layer and flow‘s direction.

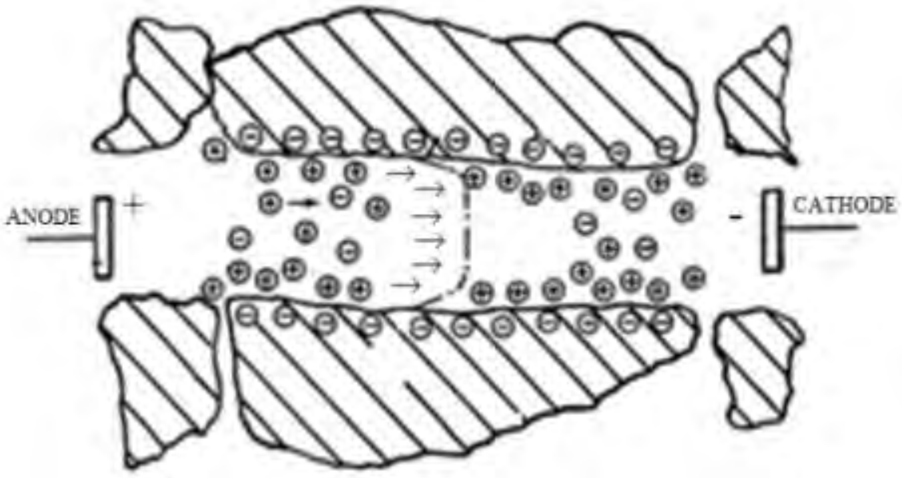


Fig. 6.2.1.1 Sketch of electroosmotic flow process. Source: Acar *et al.,* 1995.

Being in relationship with the double diffused layer, the strength of the electroosmotic flow is affected by both pore water and soil‘s characteristics. In particular, as mentioned by Virkutyte *et al* (2002), it had been demonstrated that type of minerals, zeta potential, conductivity of the fluid and temperature have great influence on electroosmotic flow. Concluding, it could be stated that electroosmosis increase with the increasing of zeta potential, with the decreasing of conductivity of the solution and by increasing the pH of the environment (Acar *et al.,* 1995; Virkutyte *et al.,* 2002). In parallel, positive relation between the strength of the electric field had been demonstrated; while, on the contrary, electroosmotic flow seems to be appreciable just for fine grained soils like clay or silts (Ferrarese *et al.,* 2008). It should be underlined that, electroosmotic processes may wrongly be assumed to comprehend also processes related to chemical osmosis that are, in facts, just related on ion‘s concentrations gradients.

6.2.2 Electromigration

Electromigration could be described as the movement of ions and polar compounds through the soil media due to the imposition of an electric gradient; more simply it could be seen as the movement of dissolved anions and cations and even polar complexes to the anode and cathode respectively. It had been demonstrated that, in comparison to electroosmosis, the induced mobility of ions on electromigration is up to 10 times greater (Morales *et al.,* 2002); for this reason it could be assumed electromigration to be the most important process concerning ionic species transport (Acar *et al.,* 1995; Morales *et al.,* 2002; Virkutyte *et al.,* 2002). Anyhow, electroosmosis and electromigration had been demonstrated to simultaneously occur (Acar *et al.,* 1995). Widely accepted electromigration models take into consideration that the migration velocity of ions (u_m) could be expressed as a function of the ion's charge of valence, gas and Faraday constants, temperature and an effective diffusion coefficient of ions parameter (Acar *et al.,* 1995). It should be underlined that more recent studies had demonstrated the relevance of both soil porosity and tortuosity while modeling electromigration (Ferrarese *et al.,* 2008). Concerning electromigration, the movement of H^+ and OH^- ions is considered to be of primary importance considering its effects on the soil matrix; it had been demonstrate that the formation of the acid and basic front are at the basis of the electrochemical remediation (Acar *et al.,* 1995; Reddy *et al.,* 2009). As it is well known, H^+ and OH^- ions are produced by electrolysis reactions as soon as water is interested by an electric current; as it could easily guessed, as soon as hydrogen and hydroxyl ions are formed they are attracted by the respective counter electrode thus causing the homogenous movement of the two fronts (Acar *et al.,* 1995; Reddy *et al.,* 2009). Reactions at electrodes could be written as:

- Anode: $2\ H_2O \rightarrow O_{2(gas)} + 4H^+ + 4e^-$ (water oxidation)
- Cathode: $2\ H_2O + 2e^- \rightarrow H_{2(gas)} + 2OH^-$ (water reduction)

It had been experimented that acidity transport is faster that the OH^- transport due to the improvement of the H^+ migration with electroosmotic reactions (Acar *et al.,* 1995; Page *et al.,* 2002) thus to decrease the pH among the two electrodes; anyhow, it could be stated that the formation of pH-change zone in the between of the soil occur depending on both electric field strength and soil buffer capacity characteristics. As it had been previously told, changes into pH greatly affects the mobility of ions, transport processes and charge conditions of soil's particles; effects of pH changes on metal's mobility will be detailed discussed in next chapters.

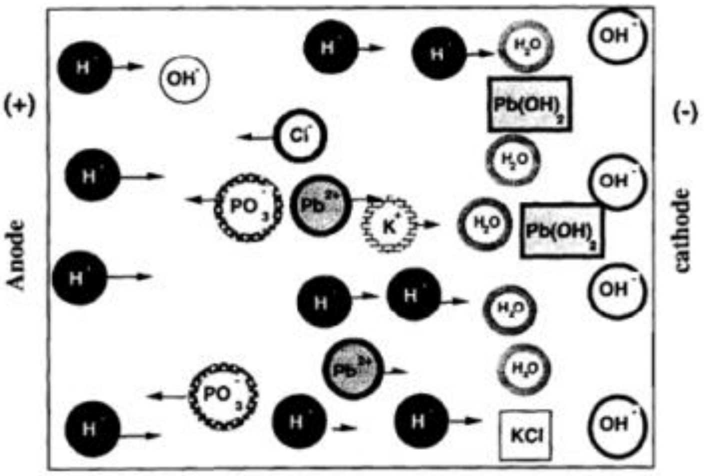


Fig. 6.2.2.1 Electromigration of ionic species and electrolysis products. Source: Acar *et al.*, 1995.

6.2.3 Electrophoresis

Electrophoresis consists in the movement of solid particles as colloids once get interested by an electric field; similarly to electromigration, particles are attracted to the opposite electrode as a function of its own orientation. Usually, electrophoresis's contribute is considered to be the less important among electrochemical phenomena (Ferrarese *et al.*, 2008; Morales *et al.*, 2002). Concluding, a graphical scheme of the transport mechanism among the soil matrix and the general framework of an ECRT is given in figure 6.2.3.1.

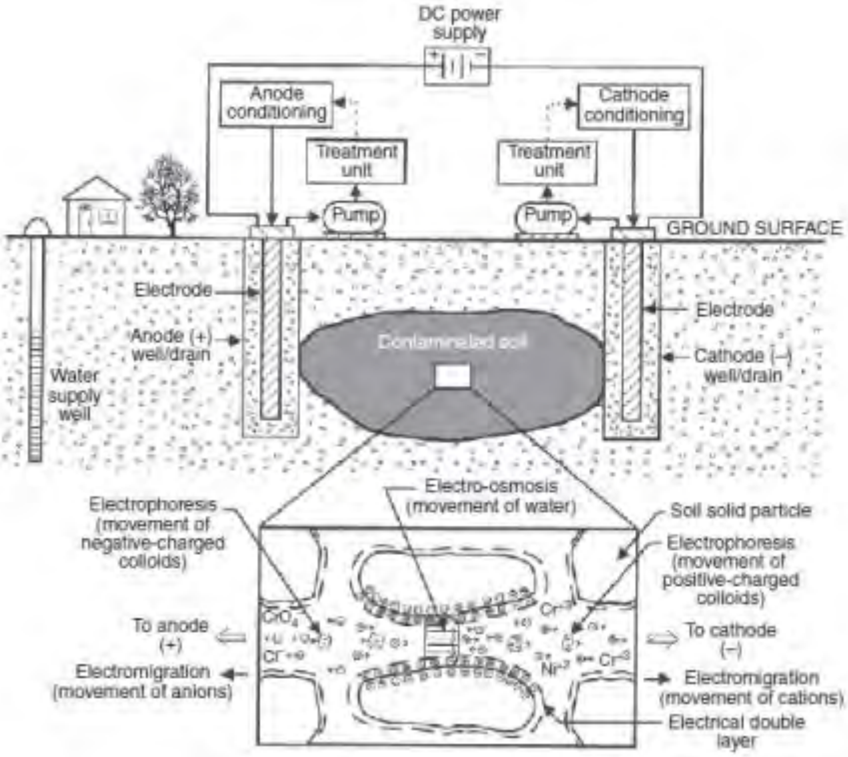


Fig. 6.2.3.1 Graphical representation of transport mechanism and electrode's position. Source: Reddy *et al.* 2009

6.3 Geochemical reactions

In parallel to transport's processes, geochemical reactions have to be taken into considerations while discussing about the ECRT mechanisms. It could be stated that, in addition to the above mentioned H^+ and OH^- front's movement, reactions of sorption/desorption, complexation, oxidation and reduction play a significant role during EC remediation. If one side it is widely accepted that most of geochemical reactions occurring during ECRT are pH depending; on the other side, it should be underlined that still nowadays electrochemical reactions in soils have not been fully understood (Reddy *et al.,* 2009). As it had been previously described, redox reactions are not localized just on the nearby of the two electrodes but diffused among the whole soil domain thanks to the microelectrodes behavior of soil particles. Moreover, as it had been reported by Ferrarese *et al.,*(2008) , oxidation reactions could occur in soils due to the diffusion of oxidant agents released during electrolysis and in function of soil's composition. More precisely, what is likely to happen is that the Iron content in soil minerals reacts with the hydrogen peroxide formed after electrolytic reactions thus releasing among the soil matrix hydroxyl's radicals (Fenton-like reaction) (Rahner *et al.,* 2002).

Concerning sorption and desorption reactions, several studies had demonstrated ECRT to be able to change mobility of inorganic compounds from polluted soils; its efficiency is mainly related to the combined effect of pH changes, complexation reactions and soil's characteristics (Acar *et al.,* 1995; Page *et al.,* 2002; Virkutyte *et al.,* 2002). As reported by Acar and other outhors, metal's mobilization occur in the nearby of the cathode due to the acid accumulation, at the same time it had been demonstrated that in the pH-change zone precipitation reaction occurs frequently.

6.4 ECRT influence factors

As it has previously discussed, ECRT is appreciated among remediation techniques thanks to its flexibility of in-situ ex-situ application both on saturated and unsaturated soils (Acar *et al.,* 1995; Virkutyte *et al.,* 2002; Reddy *et al.,* 2009). Although its versatility, ECRT had been demonstrated to be limited by several working-conditions parameters and sample features.

Concerning soil's characteristics that may affect the efficiency of ECRT, considerations have to be discussed both for soil chemistry and soil structure as reported by Page *et al* (2002). It had been demonstrated and reported by several studies that ECRT greatly depends on the size of soil particles (Acar *et al.,* 1995; Rahner *et al.,* 2002; Yukeselen *et al.,* 2012), in fact, ECRT's rates were found to be inversely proportional to grain size thus to remediate faster clays and silts than sand and gravels (Niroumand *et al.,* 2012). It seems to be reasonable to state that this behavior is related to the greater specific surface on clays than sands or gravels; as a consequence, clays are characterized by an higher surface charge density and thus a larger double diffused layer that allows grater electroosmotic and electromigrations phenomena (Acar *et al.,* 1995).

At the same time, it had been demonstrated that increasing of Cation Exchange Capacity and dissolved ions in solution induces a decrease of the ECRT‛s efficiency (Page *et al.,* 2002; Virkutyte *et al.,* 2002); in parallel, stronger adsorption processes and lower remediation targets were assessed in relation to higher organic matter content in soil. The soil‛s buffer capacity had been demonstrated to be of primary importance during ECRT as CEC, zeta potential and other soil‛s characteristics are greatly affected by pH changes (Acar *et al.,* 1995; Page *et al.,* 2002). High buffer capacity limits the ECRT efficiency due to the reduction rates of the acid front‛s movement and thus decrease the possibility of metal to get desorbed. Furthermore, high presence of Calcium, Aluminum and Iron compounds in the soil structure had been demonstrated to limit the ECRT efficiency due to the formation of metal hydroxides precipitation (Acar *et al.,* 1995; Ferrarese *et al.,* 2008). In parallel, the precipitation of metal hydroxides had been proved to clog the soil‛s pores and consequently reduce the flow within the sample. The relationships between classes of pollutants and ECRT efficiency will be treated in next chapter with a particular stress on metal‛s speciation. As could be easily guessed, the presence of pore water is one of the most important parameters during electrochemical remediation; concerning for both saturated and unsaturated soils, moisture works as a vector for pollutants removal and as conductor for electric field as well (Acar *et al.,* 1995). Experimental results had shown that under a certain moisture percentage any electromigration occur; in parallel, water content close to saturation were demonstrated to compete within the soil‛s porosity (Morales *et al.,* 2002). As it had been reported by Page *et al.,* (2002), low moisture content may lead to soil‛s shrinking and cracking due to the heating and the non-uniform water distribution among the pores. At full scale applications other parameters may be influent on ECRT, details will be discussed in costs and benefits chapter. In conclusion, in table 6.4.1 are summarized major factors that affect ECRT (Page *et al.,* 2002; Virkutyte *et al.,* 2002) and the most suitable conditions for electrochemical remediation.

Tab. 6.4.1 Most influencing parameters and suitable conditions for ECRT.

Most influencing parameters:	**Suitable conditions:**
Moisture content of the soil	limited soil’s buffer capacity
Soil’s features	low ions concentrations on pore water
pH	high soil water content
Pollutant’s features	fine grained soils

6.5 Enhanced ECRT

As it was discussed in previous chapters, ECRT is limited to be effective just on mobilizing fractions of pollutants present as dissolved ions or adsorbed forms on colloidal particles (Acar *et al.,* 1995; Virkutyte *et al.,* 2002; Yeung *et al.,* 2011). In many cases had been proved that ECRT alone was not able to reach the target‘s concentrations, thus, enhanced measures to improve pollutant‘s mobilization, transformation or breakdown of the contaminants and pH control seems to be required (Yeung *et al.,* 2011). In this paragraph will be discussed the state of the art concerning the enhanced measures, and related combinations, that could be used for pH control, mobilization of pollutants, transformation and breakdown of contaminants.

6.5.1 pH control

As it had been previously discussed, the electrolysis of water produce free H^+ and OH^- ions that tends to move respectively to the cathode and to the anode; what is likely to happen is that pH values tend to decrease significantly to the anode while increase to the cathode. As It could easily guessed, for soils with a low buffer capacity, pH-control enhanced techniques are aimed to keep the pH close to anode and cathode into appropriate ranges for pollutants removal (Yeung *et al.,* 2011); optimum pH values had been demonstrated to ensure an higher velocity of electroosmotic flow, preserve the electrode‘s conductivity and prevent the inversion of ion‘s migration as well (Ren *et al.,* 2014). Furthermore, concerning the proximity of electrodes, by pH control several undesired reactions maybe overcome:

- cathode: by raising the pH in the nearby of the cathode precipitation of carbonates and electroplating on the electrode may be limited;
- anode: by lowering the pH in proximity of the anode mobilization of metals that are not targeted as pollutants may be overcome in order to allow the removal of just desired compounds. More frequently pH values get lowered on the anode thus to promote an higher solubilization of contaminants.

Among the different possibilities, ion exchange membranes and conditioning agents had demonstrated to be the most used techniques for pH control (Ren *et al.,* 2014; Yeung *et al.,* 2011). As reported by different authors, conditioning agents had proved to be effective on As, Pb, Cu, Zn and even organic and chlorinated compounds contaminated soils (Ren *et al.,* 2014). More precisely, in addition to its improvement on pollutant‘s removal, electrode‘s conditioning with chemical agent had been demonstrated to be an effective enhanced technique for the reduction of alkalinity in the nearby of the electrodes (Puppala *et al.,* 1997); during these studies a biodegradable weak acid such as CH_3COOH was proved to a competitive alternative to other chemicals. It should be pointed out that the use of weak acids into soil or groundwater remediation could generate a secondary source of pollution (Yeung *et al.,* 2011). The pH control is assessed by the use of selective membranes that do not allow the undesired ions to pass and reach the electrode (Kim *et al.,* 2005); alkalinity regulation had been performed by cation exchange membrane thus to reduce the OH^- front‘s movement during different tests that had shown divergent results on pollutants removal as reported by Puppala *et al* in 1997. It should be underlined that these kind of enhancement are often affected by fouling of membranes and high energy consuming costs (Yeung *et al.,* 2011).

6.5.2 Mobilization of pollutants

In parallel of pH control techniques the addition of chemical agents is often used as enhancement of ECRT (Gomes *et al.,* 2012). As reported by Yeung *et al* (2011) , dealing with soils with high buffer capacity the use of enhancement agents could be seen as necessary. It could be stated that reactants are used in order to achieve both an higher solubilization of the pollutant and a more stable soluble form of the pollutant into solution. A brief description of the most common used enhancement agents is presented as follow:

- *chelating agents*: chelating agents are able to desorb pollutants (metals) from the soil and consequently form stable complexes between the pollutant and solution. At the same, it had been demonstrated that the use of chelating agents decreases the negative charge of the soil thus improving the electroosmotic mass flow to the cathode (Yeung *et al.,* 2011). EDTA, DTPA and citric acid had been demonstrated to be the most effective for metal‘s chelation during ECRT; at the same time they fulfill non-toxicity and biodegradability requirements. It should be underlined that the chelating agents have a significant cost on the cost-benefit analysis of the whole remediation; recent research studies have been developing measures to recover chemicals within the soil matix. In parallel, complexing amendments had been widely proved to be suitable for ECRT enhancing; similarly to chelating agents, with the only difference in terms of number of bonds, complexing compounds improve the formation of soluble complexes (Yeung *et al.,* 2011).

- *surfactants*: surfactants or biosurfactants are widely used as flushing solutions in order to improve the removal of hydrophobic organic compounds by enhancing their solubilization or reducing its surface tension (Gomes *et al.,* 2012; Ren *et al.,* 2014). These abilities are based on the surfactant‘s composition made of an hydrophobic and hydrophilic head and tail respectively. Anionic, cationic and non-ionic surfactants may be used during EC remediation but it should be pointed out that in function of the ionic characteristics of the used surfactant, different effects should be expected. It had been demonstrated that cationic surfactants are not suitable for EC enhancement due to their strong interaction with soil‘s particles; on the other hand, the use of anionic surfactants seems to improve the electromigration process (Gomes *et al.,* 2012). It should be remarked that the use of surfactants may be limited by the possible presence of side products during degradation, pH working conditions and its tendency to get adsorbed. As reported by Ren *et al* (2014), the use of surfactants may be combined to the synergic effects of cosolvents spreading. Concerning the effects of surfactants on heavy metals, different results had been showed through the years (Yeung *et al.,* 2011); however it seems to be reasonable to conclude that the combination of surfactants with complexing agents may give significant results.

6.5.3 Transformation and breakdown of contaminants

Unlike other EC enhancements that induce just the phase transfer of contaminants, oxidation and reduction agents are able to force the degradation, transformation or stabilization of pollutants and microbiology present into the soil matrix (Yeung *et al.,* 2011; Ren *et al.,* 2014). The injection of different reductive or oxidative agents had been demonstrated to be feasible for a wide range of both organic and inorganic pollutants; however, it could be stated that the most used techniques deal with Fenton‘s reagents, permanganate and persulfate (Yukeselen *et al.,* 2012; Ren *et al.,* 2014).

- *Fenton's agents*: Fenton‘s processes involve catalytic reactions between H_2O_2 and Fe^{2+} thus producing strong oxidizing agents as the hydroxyl radicals $OH^{\cdot}$. More precisely, the oxidation of Fe^{2+} to Fe^{3+} occur thanks to the transformation of H_2O_2 to $OH^{\cdot}$, further reactions of unspecific oxidation take place between the hydroxyl radical and the organic compounds (Yeung *et al.,* 2011; Gomes *et al.,* 2012). There are different practical solutions to add to the soil matrix H_2O_2 and Fe^{2+} reagents; injection from external sources or iron electrode sacrifice could be used as well (Ren *et al.,* 2014). It should be underlined that although Fenton‘s reactants had been demonstrated to be efficient and cost-effective (Ren *et al.,* 2014), the dependence of the process on low pH values requires parallel pH control techniques (Yeung *et al.,* 2011; Ren *et al.,* 2014). In parallel, Fenton‘s reaction are often used in combination with chelating agents in order to improve natural sources of Fe.

- *Permanganate*: as it had been reported by Ren *et al* (2014), permanganate high oxidation potential, great stability and contained costs had proved its use to be as an effective alternative to Fenton‘s reactions. Limitations of the liquid phase oxidizing agent spreading into the sample medium had been proved not be a problem even into fine particle soil (Yukeselen *et al.,* 2012). Vice versa, it had been demonstrated that, during permanganate enhanced remediation, precipitation of MnO_2 may occur and limits the further oxidation reactions (Ren *et al.,* 2014).

- *Persulfate*: it had been demonstrated to be a stronger oxidizer with a long-life effects on the soil matrix; similarly to hydrogen peroxide, once get activated, persulfate releases oxidizing radicals. Moreover, as reported by Yukeselen *et al* (2012), persulfate is able, thanks to its stability and high solubility, to reach zones of the soil far from the injection; unlike permanganate agents, any production on by-products is present during persulfate injections. Despite the contained costs of the chemical, significant activation‘s costs are related to the addition of heat, chelants, hydrogen peroxide or high pH conditions.

6.6 Combination with other remediation technologies

It could be stated that the above mentioned enhancement of electrochemical remediation may be seen as a mixed treatment of ECRT and soil flushing or soil washing; a quick overview on the possible combinations of ECRT and other soil‘s remediation techniques will be discussed in this paragraph.

Concerning bioremediation as a general technique, it could be stated that the process is based on the simultaneous presence of microorganisms (bacteria, fungi or yeast), source of energy (organic pollutants), electron acceptors and nutrients in the soil matrix; once these features are available, reactions of degradation, transformation or immobilization are performed by the biotic populations. As it had been demonstrated by Deflaun and Condee in 1997, an higher and directional dispersion of the bacterial population could be achieved once the sample get forced by a direct current; reasonably, it could be assumed that the strength of electrobioremediation is essentially related to this feature. In fact, the huge limitation on bioremediation of fine grained soils is the poor diffusion of nutrients, organisms and electron acceptors that often affects the process itself; on the contrary with an applied electric field, electromigration, electroosmosis and other transport‘s mechanism supply this scarce diffusion. Furthermore, the heating of the soil by the current flow in commonly accepted to improve any biotic reaction; it should be reminded that above 45°C bacterial reactions are inhibited (Yeung *et al.,* 2011). Electrobioremediation had been proved to be effective for both organic and inorganic pollutants; in parallel, the possibility to work in situ or on excavated samples made this combined treatment of particular interest. Vice versa, dealing with living organism this method had been proved to be limited on low polluted soils in order to not intoxicate the biotic populations. Other limitations of the electrobioremedition concern the possibility of highly toxic by-products during degradation and the kind of operational conditions that develop during the remediation (Virkutyte *et al.,* 2002; Yeung *et al.,* 2011). Even if few studies had been developed concerning phytoremediation combination with EC, recently the hypothesis to increase the mobility of pollutants by electrochemical reactions and thus improve phytoaccumulation or phytoexctraction remediation had been stressed out. More precisely, ECRT and simultaneous phytoremediation were assessed to be effective on heavy metals polluted samples (Gomes *et al.*, 2012).

Permeable Reactive Barriers are widely used as remediation techniques of ground water polluted by organics or inorganics as well (Obiri-Nyarko *et al.*, 2014); briefly, the PRB mechanism is based on the passive interception of the contaminated water flow with a cross wall made of different reactive materials. The combination of PRB and electrochemical remediation lead to the improvement of the flow across the barrier given by an electroosmotic engine rather than an hydraulic gradient. It should be underlined that, concerning remediation of fine grained soils, the enhanced transport is a result of primary importance as reactions of electroosmosis and electromigration may be considered predominant on advective flows. As it had been reported by Gomes *et al.,* 2012, different materials and configurations had been tested for PRB and ECRT combination; however, it could be stated that most of the field experience had used activated Zero Valent Iron barrier arranged into Lasagna‘s configuration. The alternation of electrodes and treatment zone used in Lasagna‘s equipment promotes reactions of sorption, immobilization and degradation to occur directly in the soil matrix; in parallel the electric field enhance the movement of pollutants among the different layers (Yeung *et al.*, 2011). The high flexibility of electrode‘s orientation, the possibility to work in situ without any excavation and the wide range of pollutants that could be removed made Lasagna configuration and PRB in general a promising combined technique with ECRT (Yeung *et al.*, 2011; Gomes *et al.*, 2012; Ren *et al.*, 2014). On the other hand it should be pointed out that pH changes induced by ECRT affect both sorption and degradation rates of most of the reactive barrier materials; similarly the use of chemical enhancement for electrochemical remediation may compete or limit the efficiency of PRB mechanism.

Other remediation technologies had been coupled with electrochemical remediation but still nowadays further researches have to be carried out. Briefly, tests were performed into thermal desorption aided with electric field in order to promote both physical and biological reactions of desorption, solubilization or degradation; any valuable result was available. Few studies were focused into the combined effects of electrochemical remediation and ultrasonic wave imposition in order to force destruction of hydrophobic pollutants by cavitation‘s phenomena; results had showed that this enhanced technique is limited to low percentages of pollutant‘s removal (Gomes *et al.*, 2012). Oxidation phenomena had been found to be achievable by the electrification of anode alone in the soil matrix; even if it had been demonstrated to have localized and poor efficiency, this solution allows to prevent further enhancement for hydroxide‘s control, to handle the equipment with more simplicity and to avoid larger use of chemicals (Yeung *et al.*, 2011). Concluding, it could be stated that electrochemical remediation enhancement had been proved to be effective and promising techniques for both organics and inorganics removal. The combination of ECRT with other techniques provides a great innovation for fine grained polluted soils but further studies had to be carried out.

In order to summarize the possibilities on ECRT enhancement and coupling the following graphical scheme is reported.

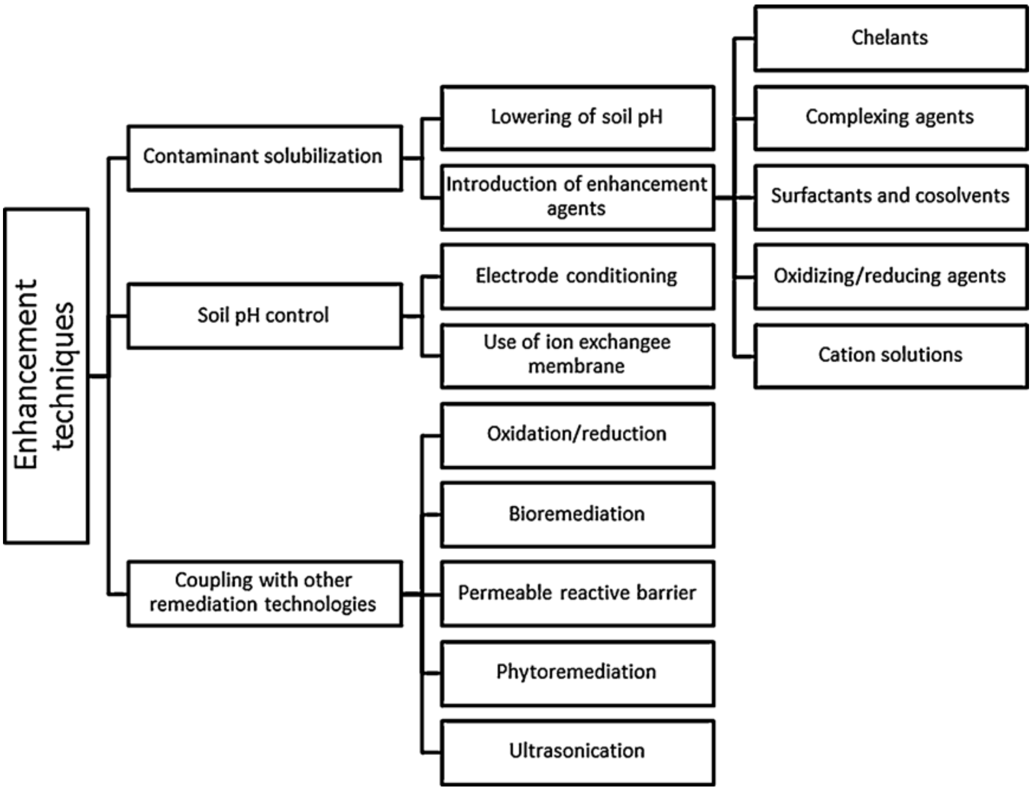


Fig. 6.6.1 Graphical summary of ECRT's enhancement and coupling technologies. Source: Yeung *et al.*, 2011.

6.7 ECRT state of the art

In this paragraph an overview of the most significant results obtained for metal's removal will be summarized for both bench scale and field scale experiences; at the same time, the literature review had been chosen to be presented into chronological order in order to check out the ECRT evolution. Particular attention will be given to differences evidenced during the scale up of the test and to the great differences on efficiencies that may be found while working with artificial soil or naturally contaminated samples.

Li *et al.*, 1996 during their experience had tested that up to the 96% of the total metal concentration could be achieved thanks to the addition of a conditioning agent at the cathode compartment. The lab scale experiment was set with a cylinder of 30cm length and 35mm of diameter filled up with sandy soil in contact with deionized water or electrolytic solution. Graphite disk electrodes were used and a constant DC of 30V was applied. Concentrations of both copper and zinc were obtained by the addition of chemical amendments to the soil. During the test was proved that removal efficiency (calculated within 1 week of time span) greatly depends on the presence of the conditioning agent and the conductive solution; however, ECRT was demonstrated to be able to induce Cu and Zn removal. It should be pointed out that artificially spiked sandy soil present lower binding forces due to the lack of organic matter and clay particles absence.

Similarly, Mohamed *et al.*,1997 was able to prove the removal of several different metal occurring simultaneously. The test was conducted by the use of stainless steel electrodes into an electrokinetic cell of 76 mm diameter and 267 mm/133 mm length; maximum current applied was 3A with a DC of 30V. Soil used for the test were taken from two polluted sites and were found to be both loose silty sand with considerable differences into percentages of impurities and organic matter. Even in this case different conditioning reagents were used in order to promote metal desorption and removal efficiencies were proved to be in function of the kind of used solution; results had showed that Ni, Cr, Cd had been removed with efficiencies close to 90% for both the soil sample, on the contrary the majority of the other metals (Cu, Cr, Ca, Pb, Zn) was removed with significant discrepancies within the two soil samples. Authors explain this behavior to be related to initial concentration, type of soil and kind of soil‘s properties.

A comparison between the removal efficiencies from an artificial spiked soil and naturally contaminated soil was performed by Kim *et al.,* 2000; during the lab experience mobilization of Cd and Pb were evaluated. Over four days of test duration the applied current was constant at 0,1 A, platinum wire and titanium plate were used respectively for anode and cathode compartments. Almost 1,215 cm^3 undergone to the applied current in each of the three test that had carried out with the application of H_2SO_4 solution. Spiked soil were tested separately for Pb and Cd removal, while for the tailing soil just one run was carried out; results had showed Cd removal efficiencies of 86% and 68% respectively for spiked clay and tailing soil, while Pb removal efficiencies of 75% and 50% were asses. Lower efficiencies in tailing soils were demonstrated to be associated to an higher buffer capacity and to presence of other natural competitors ions.

Great removal efficiencies of Cr were experience by Sawada *et al.,* 2004 from an artificially spiked kaolinite thanks to the presence of an adsorbent media; in parallel, Gent *et al.,* 2004 had proved both on bench scale and pilot scale significant Cr and Cd removal. During the 1,200 h of bench scale duration 5 A/m^2 were adopted, while field case had been performed for four months at 10-17 A/m^2. Authors had reported that during this study was experienced that higher removal efficiencies were related to the field case rather than to the lab scale. Lower rates of removal were thought to be limited by the short length of the sample and by the impacts of the boundaries.

Lead removal into pilot scale modules was experimented by Alshawabkeh *et al.,* 2005 and promising results were obtained. In particular, modules were build up as 76cm width, 91cm depth, 183cm length properly sealed and filled with contaminated clayey sand and sandy soil; graphite and galvanized iron were used for anode and cathodes respectively. Current densities had been modified during the test by doubling the parameter after 112 days of treatment; initial current was set at 0.6 A with a voltage of 292 V, by doubling the current at 1.2 A the voltage rise to 200 V. Even in this test, pH conditioning was used in order to avoid accumulation at the cathode during the 9 to 11 months of pilot scale experience. At the end of the test, lead removal

efficiencies of 85% and 70% were asses on top sandy soil and deeper clayey soil respectively; at the same time, Alshawabkeh and his working team had found that accumulation at the cathode was likely to occur even in the presence of the conditioning agents. The pilot scale seemed to be limited by the fact that other pollutants (Cu) had been mobilized but not extracted; so, accurate speciation analysis and adequate period of remediation should be accurately evaluated. The promising results of a full scale ECRT application had been asses also by Wieckzorek *et al.,* 2005 by a preliminary study at lab scale; efficiencies up to 60% were experienced for nickel.
By this brief literature review, it seems that ECRT has a great ability on metal‘s remediation both on lab scale and pilot scale experiences; but, it should be pointed out that any of the mentioned results had been evaluated in light of speciation analysis. This lack may confuse during the scale up of the application and led to high cost for remediation. More recently, Garcia-Rubio *et al.,* 2011 had demonstrated the importance of fractionation as a preliminary tool for the scale up; as it could be easily guessed speciation seems to be a fundamental step during ECRT engineering.

6.8 Advantages, drawbacks and cost analysis

In order to conclude this brief overview on the main features of ECRT, a quick summary concerning advantages and drawbacks will be presented; consequently, by literature references, will be reported a cost‘s introduction of the technique.

As it had previously mentioned, the versatility of ECRT to be used on both in situ and ex situ conditions is one of the most interesting feature of the technique; at the same time, the possibility to have effective results both on saturated and unsaturated soils improves the range of application of the remediation. Furthermore, as demonstrated by several studies, electrochemical remediation had been proved to be applicable to fine grained clayey- silty soils thus overcoming the huge limitation of similar remediation techniques for heavy metals and organic pollution. Nevertheless, several studies had proved the effectiveness of ECRT on radionuclides removal. As it had been suggested by Reddy and Cameselle (2009), ECRT had received particular interest also for the possibility of combining the electrochemical remediation with several other technologies. Although the quite simple equipment and in seeming robust and simple process, great limitations were found to affect the electrochemical remediation. First of all it should be pointed out that, even if several lab scale experiences had given positive and interesting results, full scale applications are still nowadays matter of controversy (Page *et al.,* 2002). As stated by different authors, several problems that were not affecting the lab scale test became of primary importance while working at field conditions due to the high sensitivity of the technique (Page *et al.,* 2002). In particular, as it had been reported by USAEC (2000), natural occurring ions in field conditions behave differently than in lab test; the presence of heterogeneities among the soil may limit the transport of pollutant or create preferential pathways as well; chemical and biological composition of the soil itself, such as strong buffer capacity and strong organic composition,

may limit the electrochemical remediation. At the same time, it should be underlined the possible formation of toxic by-products as a consequence of the electric field imposition or in relation to the heating of the soil by the current‘s passage. As it could be easily guessed, due to the high dependence on pH of the process, the addition of chemicals seems to be required thus increasing the remediation‘s costs; in parallel, the required use of the electrolytic solution may have great impact on the overall costs. Concerning the cost analysis on electrochemical remediation, by literature review ECRT had often described to be a cost effective technique both in terms of energy consumption and chemical amendments. As the few cost analysis that were available suggest, it could be generally assumed that the most influencing parameters on the remediation costs, for a lab scale experience, are related to soil characteristics, contaminant concentrations, concentrations of non-target ions, conductivity of the pore water, depth of the remediated soil, site preparation requirements and electricity and labor costs (Virkutyte *et al.,* 2002). On the other hand, concerning field scale applications, slightly different considerations had to be taken into considerations; in fact, in addition to the soil properties and depth of contamination, costs related to the electrodes installation, the electrical power consume and the clean-up time have a great importance on the feasibility of the application (Virkutyte *et al.,* 2002).
Past studies (Ho *et al.,* 1997) had approximated that, for a field application, almost the 40% of the overall cost is represented by the electrode‘s construction, while just the 16-17% is required for energy supply and 17% for materials. Data from USAEC (2000) field experience, suggest a unit cost of almost 1,500 $\$/m^3$ for chromium and cadmium remediation. A more recent cost evaluation performed on almost 350 m^3 contaminated sediments by PAH, Mercury and Phenols (EPA.,2007), had estimated an overall cost of about 400,000 $ for 6 month of duration over 1.5 m of depth. More precisely: almost the 35% of the total cost was covered by sampling tests, start-up, installation and electrode preparation while just 1% was assigned to energy consumption. However, due to the high variability of soil‘s composition that may be found on the contaminated site seems hardly to give an unique cost‘s trend; on the other hand, as it will be demonstrated by the following study case, an accurate and detailed pollutant‘s speciation campaign could give essential information about the feasibility and thus the order of magnitude of the remediation‘s cost.

7. STUDY CASE

Now on it will be discussed the ECRT project that had been engineered for the remediation of the VP_38 Mercury contaminated spot; particular stress will be given on the speciation analysis in order to point out how decisive is the relation between the feasibility of the remediation, the legislation limits and the proper nature of the pollutants.

7.1 VP_38 site's characterization

The VP_38 spot is confined by the Lusore canal and the railway on its northern part, as it could be seen in chapter x.y, the area had been found to be heavily polluted by Mercury on the backfill soil down to 1.5m. Soil characterization was presented in chapter 4, in parallel, the literature study developed by the university of Ferrara (Rosestolato *et al.,* 2015) had confirmed the presence of four main layered structures:

- Heterogeneous, backfill soils and material present from top soil quote to an averaged depth of 5.5m. It is composed by sandy material mixed to cobbles, gravel, clay, silt and organic materials.

- Waterproof upper level with an averaged thickness of 4 m. It is composed by gray-brownish colored clays mixed with few percentages of silts; compact clayey silts mixed with few percentages of sands; brown peats of silt and clayey nature.

- First aquifer composed by fine grained gray sands with few percentages of silts; it extends for an averaged thickness of 5 m.

- Second aquifer of a variable extent from 1m to 8 m, below the 14–16.2 m from the top soil quote. Its composition is mainly characterized by gray silts and clayey silts.

The area, as it could be seen from the figure 7.1.1, had been assigned to in situ treatment and to the removal of the top soil part (20 cm from the surface); pictures of the area are presented in figures 7.1.2 and 7.1.3.

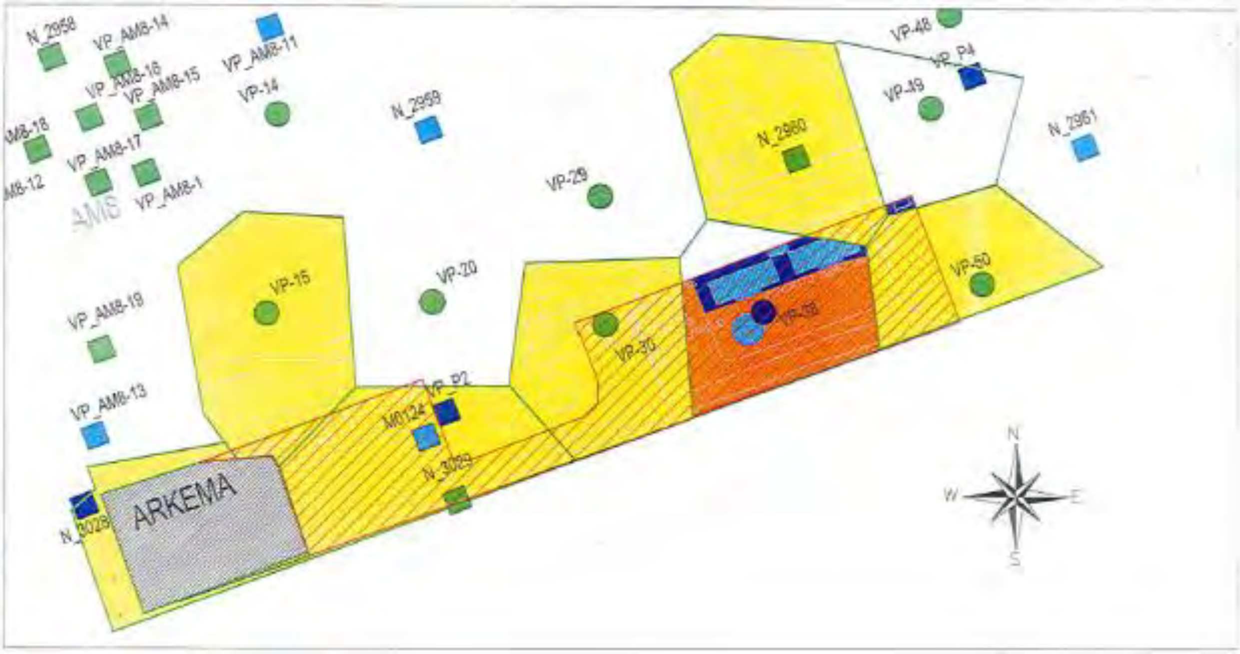


Fig. 7.1.1 Extrapolation of the Vecchio Petrolchimico area. Orange color stands for in situ treatment, Blue color stands for top soil removal. Source: SYNDIAL, SNAMPROGETTI 2006.

As it had been previously mentioned, during the characterization, concentrations above law limits of PCB, dioxins and metals had often been found from ground level to shallow depths. So, operations on top soil (20 cm depth) are aimed to remove any possibility of dermic contact with the source of pollution; the excavated soil had been temporary stored on the site and covered by LDPE sheets, at the same time proper measures to avoid any leaching on the ground were taken. In parallel, measurements of volatile compounds from the soil had given negative results. Once top soil had been removed geotextile layer had been disposed to separate new soil form old and deeper soil and to leave a mark of the remediation to following management.

Fig. 7.1.2 Excavation and temporary disposal operations on VP_38 site.

Fig. 7.1.3 Excavation and temporary disposal conclusion on VP_38 site

On the other hand, the ECRT project was planned to work on the unsaturated part of the soil; target concentration of the remediation had been calculated as reported by Eni-Snamprogetti (October, 2005). It should be underlined that the legislative procedure that was followed by the author of the analysis was considered to be inconsistent with the 471/99 decree and thus new and more conservative values were imposed by the Ministry. More precisely, target concentrations were asses by the risk analysis before the on-site evaluation of the efficiency of the remediation technique; so, the risk assessment procedure was based just on literature and theoretical results rather than the real residue concentration.

The study was conducted just on unsaturated media by the use of RBCA software and utilizing characterization‘s results proposed in previous chapters. APAT guidelines on risk assessment were followed in combination with variations concerning transport phenomena from superficial soils and carcinogenic limit (assumed equal to 10^{-5}). The analysis was performed for the whole set of compounds that were found to be higher than the law limits during the characterization of the site; non carcinogenic compounds were associated with a risk quotient (ratio between PEC and PNEC) equal to 1. Dermal contact and ingestion, outdoor vapor inhalation and indoor vapor inhalation were considered as routes of exposure for workers and operators; in parallel, soil parameters were approximated to sandy soil features. Input concentrations (as residue concentration) were assumed to be 10 times higher than the law limits reported in the 471/99 decree. Outputs form the software reveals a target concentration of 18 mg/kg Hgtot/d.m.; the Ministry had reduced this value to 13 mg/kg Hgtot/d.m.. Later on, it will be evident the importance of an accurate and more specific risk analysis based on speciation campaign.

7.2 Electrochemical remediation of Mercury contaminated soil

Due to the low solubility of Mercury, ECRT applications on Mercury contaminated soils were affected by great limitations (Cox *et al.,* 1996); more recently, thanks to the use of chemical amendments the electrochemical process seems to be effective (Reddy *et al.,* 2003; Shen *et al.,* 2009). In particular, the use of I_2/I^- lixiviant solution had been proved to increase the solubility of metallic Mercury compounds and thus promote its removal by electrochemical remediation (Cox *et al.,* 1996; Reddy *et al.,* 2003; Shen *et al.,* 2009). The bench-scale experience of Reddy *et al., 2*003 had proved that, dealing with clayey spiked soil, the best removal efficiencies (97% of the initial concentration) were obtained with a 0.1 M KI solution at 1 Volt/cm of direct current gradient; in parallel, by using similar voltages, the test conducted on a contaminated soil from a mine (Negrete *et al.,* 2013) had demonstrated the ability of the KI-enhanced ECRT to remove different Mercury forms.

7.2.1 VP_38 remediation tests: lab scale ECRT

The bench-scale experience by Rosestolato and his study team in 2004 was performed on almost 400 kg of polluted soil coming from the VP_38 site; the aim of the test was to prove the removal of polarizable species of pollutants (metallic Mercury and other species) by the imposition of an electric field and the addition of a complexing agent (KI). Geologic characterization of the soil sample had been reminded at the beginning of this chapter, however, further analysis performed by Rosestolato and his study team had given the following results about the undersieved fraction (≤ 2mm) soil samples that were collected at 0.95m depth:

Tab.7.2.1.1 Soil properties. Source: Rosestolato *et al.,* 2015

Property	Result
Soil texture	Clayed-sandy soil
Water content	13,6%
Organic content	Negligible
pH	8.2
Resistivity, water saturated	56 Ωm

Concerning the pollution characterization on the soil, accurate speciation of Mercury was conducted in parallel in two laboratories by the Boszke‘s method; the analysis were performed by combination of sequential extraction method and thermo desorption stage to determine elemental Mercury (Boszke *et al.,* 2008). More precisely, during the sequential extraction agents that were used on the subsequent stages were solutions of chloroform, deionized water, HCl, NaOH and aqua regia.

Total Mercury concentrations were calculated by EPA 7473 method and compared with the speciation results. It should be pointed out that, concerning the Italian legislation and scientific regulation, any standardized method is present for the Mercury speciation; this lack of uniformity may led to controversy during project‘s evaluation and feasibility. By speciation analysis it had been found that:

- Ranges between 2% and 8% of the total Mercury could be considered ‗easily extractable‘ fraction;
- Almost the 89% of the total represents the ‗non extractable‘ species (metallic and residual);

Among the ‗non extractable‘ fraction, almost the 44%-61% of the total is considered to be metallic Mercury, while insoluble forms are estimated between 28% and 39%. The considerable amount of metallic Mercury (almost 15 mg/kg d.w. and 10 mg/kg d.w.) sounds like an alarm bell for the risk related to possible routes of exposure. With the omission of standard deviation‘s values, results are summarized in table 7.2.1.2.

Tab. 7.2.1.2 Boszke speciation method results.

Fraction	**Lab.1**	**Lab.2**
	Hg (mg/kg d.w.)	Hg (mg/kg d.w.)
Total Mercury (EPA7473)	25.00	22.36
Organo Mercury	0.038	N.A.
Soluble in water	0.28	0.192
Soluble in acid	0.414	0.134
Humic matter	1.214	0.123
Metallic Mercury	15.27	9.808
Residual	6.87	8.703

The bench scale application was set up with 0.2 m^3 of soil into an HDPE box; electrodes of activated titanium were placed in couples on the opposite side of the container while in the middle inspection wells were accommodated. A sketch of the setup is present in figure 7.2.1.1.

The soil sample had been fully saturated with water at first in order to check out the presence of mobile pollutants, later the soil was dried and saturated with the KI complexing solution. By the use of iodides solution the aim was to obtain a stable complex (HgI_4^{2-}) that has higher solubility and moves though the anode compartment once forced by the electric field. More precisely, once the metallic Mercury is forced by an electric field it behaves like a bipolar electrode (Rosestolato et al., 2015) and undergoes to dissolution process; in the presence of KI solution, the iodide ions combine with Mercury thus creating HgI_4^{2-}. Concerning the hydraulic management of the solution, it has to be reminded that during this test the solution was recirculate in continuum. More precisely, the electrolyte solution (0.1 M of KI initially at pH = 3) was recirculate between the four electrodes with a 50 l/h flowrate; authors confirms that with this kind of system less pH adjustment were required in comparison to classic extraction configurations.

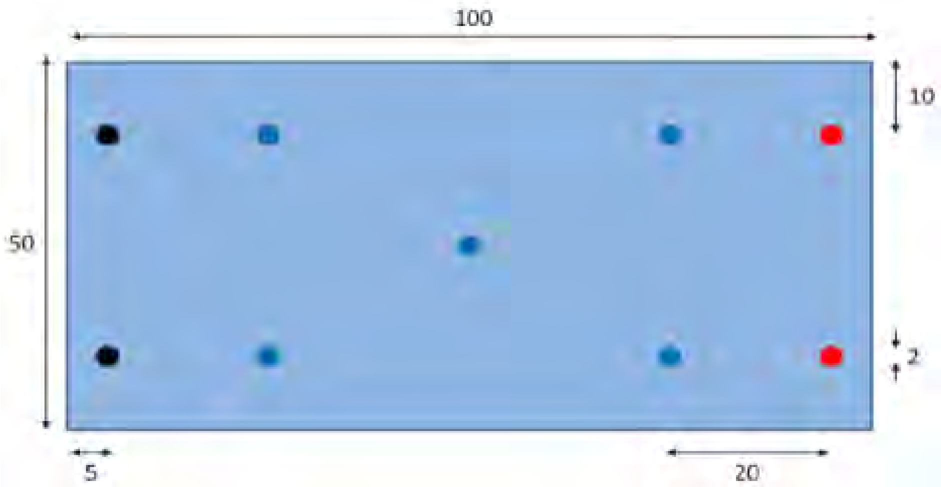


Fig.7.2.1.1 Setup of the electrodes (red-black dots) and wells (blue dots) disposition. Distances expressed in cm.

Fig. 7.2.1.2 Setup of the bench-scale ECRT and particular of activated titanium electrode.

The application (figure 7.2.1.2) had run for two months and a half, during this period different kind of voltages and currents were tested (from 20 V to 40 V and from 0.1 A to 1 A respectively). In parallel, the removal and replacement of the exhausted electrolyte solution was performed with a different frequency (after two weeks and at the end of the month). Tests on Mercury concentration were carried out on both the solutions taken from the monitoring wells and electrodes. Further analysis were performed on the tap water used to wash out (1 hour of contact) the contaminated soil in the end of the two months and a half period. As previously mentioned, pH adjustments required during the duration of the test were assessed by the addition of proper quantities of 0.1 M nitric acid solution. Analytical results of the extracted solution confirms the hypothesis that the major the Mercury had been mobilized or removed from the soil sample; at the same time, by the analysis of the water used for the washing out of the soil, a considerable fraction was still present. More precisely, removed Mercury were in the ranges of 19.2 mg to 35.4 mg respectively at 0.2A-0.3A; 16-24 V and 0.3 A; 20 3 V. Results and parameters are summarized in table 7.2.1.3.

Tab. 7.2.1.3. Results and parameters of bench scale ECRT.

Duration	Dewatering	Removed volume (l)	Hg Concentration (ppm)	Hg removed (mg)	Current and voltages
06/04 – 26/04	26/04	5.5	~0.5	2.75	0.1÷0.2A; 21÷39V
28/04 – 05/05	05/05	~6	0.73	4.38	0.2A; 26.6V
05/05 – 17/05	17/05	6	3.13	18.78	0.2÷0.3A; 21÷32V
17/05 – 31/05	31/05	~6	3.2	19.2	0.2÷0.3A; 16÷24V
31/05 – 14/06	14/06	6	5.9	35.4	0.3A; 20.3V
14/06 – 25/06	21/06	0.01	10.8	0.108	1A; 49÷60V
	25/06	6	7.78	46.68	1A; 49÷60V
Wash out	28/06	5	7.47	37.35	---
		5	5.94	29.7	
		5	2.90	14.5	

At the end of the duration of bench scale application, a new speciation was carried out on the treated soil sample by following the EPA 3200 method, considered to be more time saving than Boszke's sequential extraction. Results are summarized in table 7.2.1.4.

Tab. 7.2.1.4 EPA3200 analysis after the ECRT remediation; total Mercury calculated by AMA254 device.

Fraction	Hg (mg/kg d.w.)
Total Mercury (AMA254)	8.56
Extractable Mercury	Negligible
Semi-mobile Mercury (Hg^0)	4.11
Non-mobile Mercury	3.23

As it could be seen from the presented data, a significant removal of the total Mercury had been achieved (60%) and final concentration of 8.56 mg/kg d.w. was assessed. At the same time it should be underlined that the metallic Mercury fraction still compose almost the 55% of the total amount of Mercury; on the contrary, insoluble salts of Mercury represent about the 45% of the total amount. Evidently, a complete removal of the metallic Mercury was not achieved but it should be pointed out that the duration of the test was define in advance and any relation with removal efficiency was planned. In parallel, looking at the concentration of the residual fraction of the first speciation, considered to be the insoluble part of the total amount, it could be stated that mobiliziation of this fraction occur (from 6.87 mg/kg d.w. to 3.23 mg/kg d.w.). Furthermore, it should be underlined that results obtained from soil sample solution‘s extraction and from soil‘s speciation differs in terms of removed Mercury; authors assess the reason of this discrepancy on the set of absorption, adsorption, precipitation and electrodeposition reactions occurring in the soil speciemen.

Concluding, it could be stated that the hydraulic regime used during the pilot scale test had positive results; more precisely, the continuous recirculation system from the extraction wells and the applied electric field works as the combination of ECRT and soil washing remediation. Furthermore, thanks to the innovative recirculation system, even at low voltage electric field appreciable removal were achieved in a short time duration period. Based on the obtained results the scale up of the ECRT configuration had been engineered on VP_38 site; unfortunately, as it will be explained in the next chapter, when moving from lab scale to real scale the technique has to face with its own limitations and with a narrow minded legislation.

7.2.2 VP_38 remediation test: real scale ECRT

Now on, pilot scale ECRT that had been applied (2007/2008) in three different spots in the ‗Vecchio Petrolchimico'' site will be presented; details of the application will be presented just for VP_110 that was found to be the only effective arrangement. In parallel, it should be underlined that concerning the VP_38 remediation a slightly improved ECRT application had been engineered, in light of the recent research performed by the University of Ferrara with the collaboration of Syndial.

In order to test the efficiency of the ECRT application on Mercury removal, it was chosen to use three modules as pilot scale experiences in three different spots within the area; modules were each arranged into different configuration in order to evaluate the most suitable one. Geological characterization of the spots had confirmed the presence of a layering structure composed by backfill soil (0-5.6 m depth) and impermeable materials (6 m depth); it should be underlined that the level of the backfill groundwater table is about at 1m depth. On the other hand, concerning the contaminated spots a brief environmental characterization could be described as follow. The VP_110 had been found to be contaminate both on backfill soil and first impermeable layer with Mercury (0.15-1.5 m; 121 mg/kg), Vinyl chloride (3.1-4.15 m; 1.4 mg/kg), Dichloroethyline (4.15-5.3 m; 1.78 mg/kg), Vinyl chloride (4.15-5.3 m; 3.9 mg/kg), Dichloroethyline (5.3-5.8 m; 2.2 mg/kg) and Vinyl chloride (5.3-5.8 m; 4.6 mg/kg); the N_2613 had been found to be contaminated both on backfill soil and first impermeable layer with Mercury (0-1 m; 12.44

mg/kg), total PCB (0-1 m; 7.94 mg/kg) and Dichloroethane (7.5-8 m; 76.3 mg/kg) respectively. N_2749 site was found to have Mercury concentrations lower than law limits were found in this spot. It should be pointed out in advance that any speciation analysis was performed before the remediation application on the site; concentrations were evaluated just as total Mercury form. At the same time significant discontinuities related to peak concentrations were found in each spot so results of the technology are limited just on the portion of soil that had been treated and not to the entire polygon.

7.2.2.1 VP_110 module

On this spot the *Holland environment* ECRT patent had been used over an area of almost 50 m^2 (7 m length, 7 m width) by reaching almost 1.5 m in depth; electrodes were arranged at a mutual distance of 1.25 m and 1.25 m from the contiguous raw. Four rows of cathode (7 activated titanium cathodes each) were alternated by three rows of anodes (7 carbon steel anodes each) as it could be seen form figure 7.2.2.1.1.

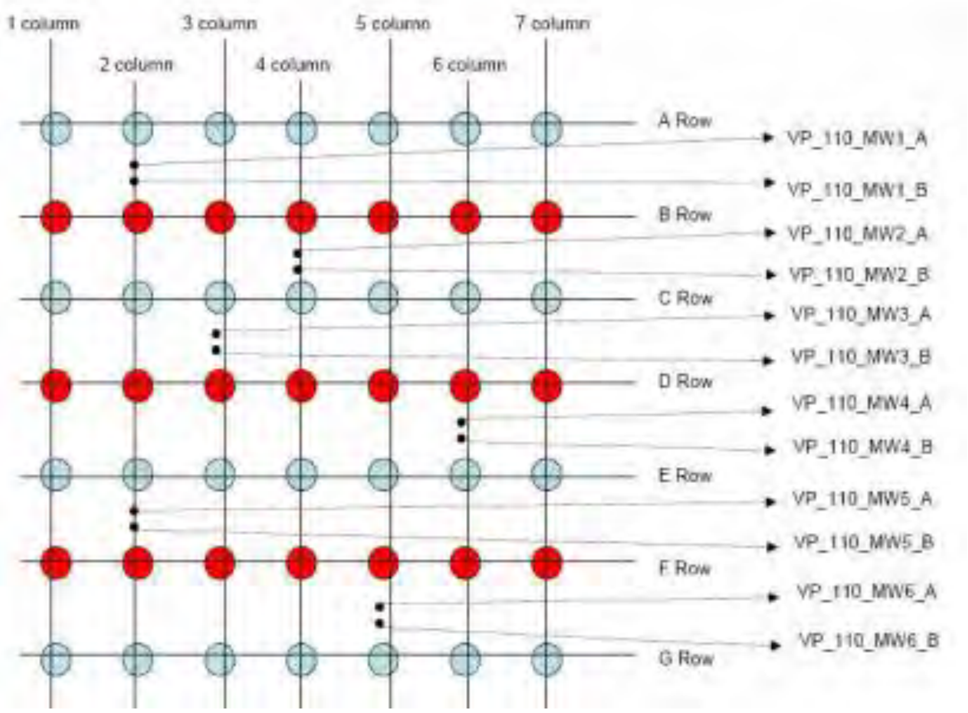


Fig. 7.2.2.1.1 Electrode arrangement. Red dots as asnodes, blu dots as chatodes, black dots as monitoring wells. Source: Progetto definitivo di bonifica dei terreni contaminate con misure di sicurezza area vecchio pertrolchimico, 2008

More in detail, electrodes were thought to be inserted into a ions-permeable casing that allows the entering ions to came in contact with the NaI electrolytic solution and thus removed by the circulation system of the solution; thus, the interaction between ions (forced by electromigration phenomena) and electrolytic solution (pumped by the circulation system) is forced to occur inside the casing thus limiting solution losses and soluble-Mercury forms spreading; in parallel, anode compartments were pumped by an HNO_3 solution. Electrodes diameter range from 18 cm (from 1 m to 0.5 m) to 9 cm (-0.5 m to 0 m) while the casing diameter is fixed at 29.8 cm; the void space between the casing and electrode was filled up, from the bottom up to ground surface, with 2mm-3,5mm gravel and dusted clay. Monitoring wells were inserted among the ECRT area in order to assess the evolution of the remediation by the analysis of both superficial groundwater and soil in the nearby of the groundwater wells; each well was composed by a PVC tube filled up with 2 mm -3.5 mm gravel. Concerning the setup of the ECRT module, main features may be described as the Electrode supply unit (ESU) that contains the power supply unit used to feed electrodes, pumps and other devices; the Envirocell unit (ECU) that contains the electrolithic cell required for Mercury reduction and removal; the Water treatment unit (WTU) that works for the pH conditioning of the electrolyte before the solution recirculation. As it could be seen in figure 7.2.2.1.2, once the voltage gradient is applied at the electrodes (89 V-35 A) the system works by pumping and treating the Mercury-iodine solution from each cathode compartment to the Envirocell in order to recover the electrolyte and remove Hg; the output solution is further stored and pH conditioned before its recirculation among the cathodes.

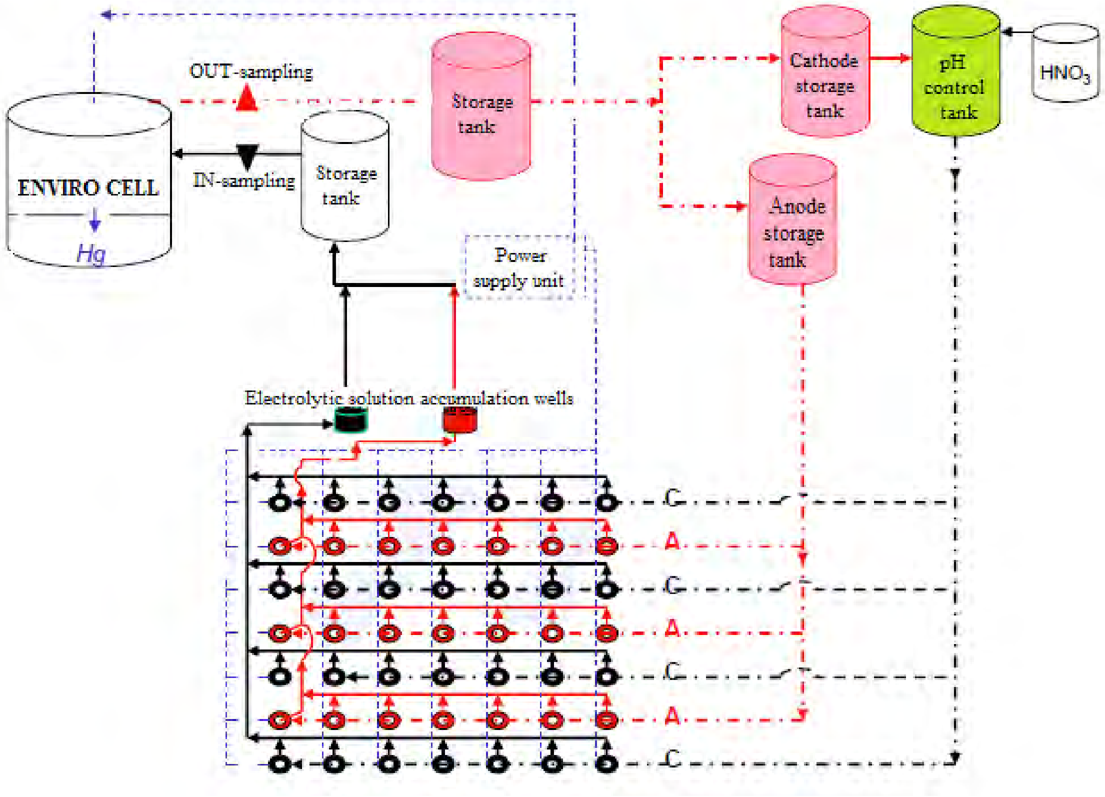


Fig. 7.2.2.1.2. Lay out of the VP_110 ECRT application. Source: Progetto definitivo di bonifica dei terreni contaminate con misure di sicurezza area vecchio pertrolchimico, 2008

During the remediation period both soil and groundwater samples were analyzed in order to assess the effectiveness of the technique (D‘Emilio et al., 2008). As it could be seen in table 7.2.2.1.1, after 6 months of treatment each soil sample was found to be lower than the required law limits; on the other hand, the concentration's trend in function of time did not seem to follow a linear behavior.

Tab. 7.2.2.1.1 Mercury concentration in soil samples during the remediation. Source: D'Emilio *et al.,* 2008

Sampling points	U.M.	Campaing S1	Campaign S2	Campaign S3	Campaign S4
VP_110_MW1	mgHg/kgTS	12.9	13.6	8.2	2.7
VP_110_MW2	mgHg/kgTS	4.8	10.3	3.4	3.2
VP_110_MW3	mgHg/kg TS	3.0	4.6	11.2	2.9
VP_110_MW4	mgHg/kgTS	6.9	13.3	17.6	2.1
VP_110_MW5	mgHg/kgTS	7.0	4.2	<0.1	4.6
VP_110_MW6	mgHg/kgTS	3.2	56	12.8	2.7

Concluding, thanks to the application of VP_110 module researchers were able to conclude that: the iodine solution was able to force Hg mobilization; soluble fractions of Hg were transported both at anode and cathode compartments by following different pathways; recovery of Mercury was possible outside the system and the application was able to remediate polluted soil samples.

7.2.2.2 N_2613 module

The remediation of this spot was engineered by Lyntech with an ECRT application similar to the VP_110 one. The net of electrodes covered a surface of almost 200 m^2 thanks to the presence of two rows of anodes spaced out by one row of cathodes; the distance between electrodes of the same row was fixed at 5 m both for cathodes and anodes (three and two for each row respectively) while the distance between anodes and cathodes raw was 10 m. Ennobled titanium net electrodes were inserted at 1m depth surrounded by PVC slotted cases of 110 mm internal diameter; each slotted pipe had been covered by a geotextile material in order to avoid the accumulation of fine grained particles into the casing. Furthermore, electrode's casings were thought to be equipped by an electrolyte solution recirculation system composed by:

- Pipes for electrolyte addition to casings (both at cathodes and anodes), pipes for mercury-enriched electrolyte removal (just at cahodes);
- Level's detector for solution addition (both at cathodes and anodes) and centrifuge pump, level's detector for solution removal (just at cathodes) and centrifuge pump.

In parallel, the recirculation system was composed by accumulation tanks for both solutions to be added at the cathode and anode and for the extracted solution from the cathode. A schematic representation of the ECRT configuration is presented in figure 7.2.2.2.1.

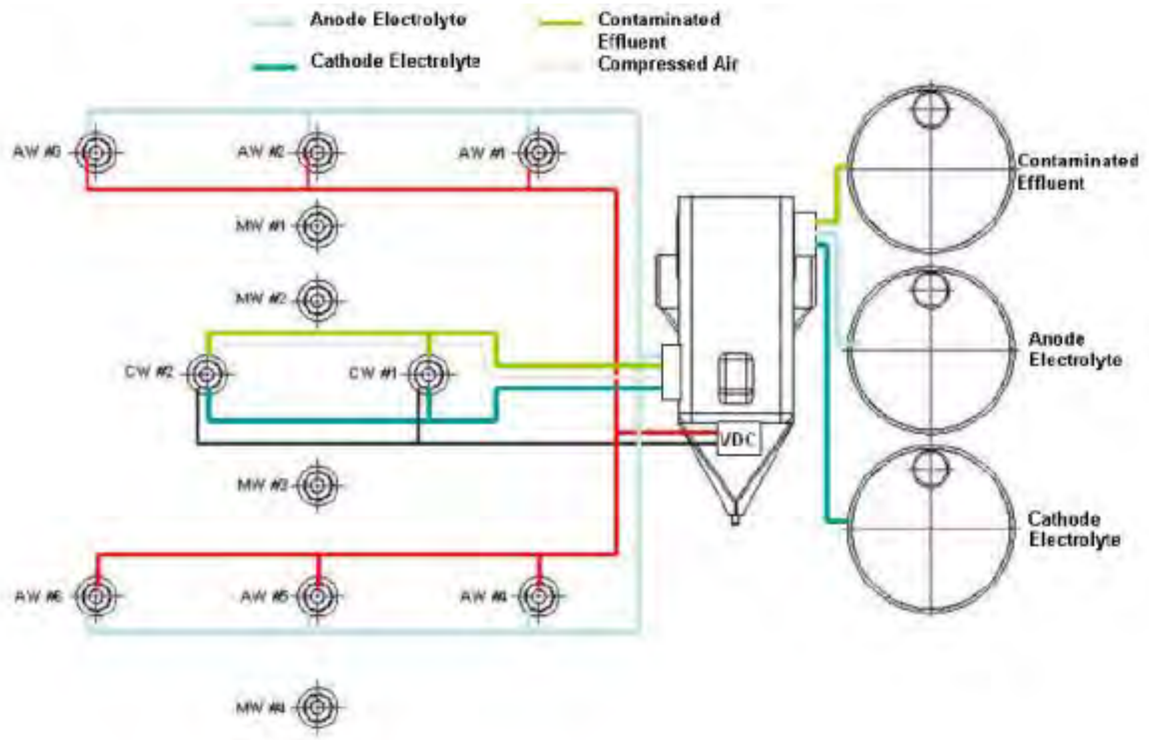


Fig. 7.2.2.2.1. Lay out of the N_2613 ECRT application. Source: Progetto definitivo di bonifica dei terreni contaminate con misure di sicurezza area vecchio pertrolchimico, 2008

Concerning the electrolyte solution, Lynetech prescribe the use of compounds able to modify the electrokinethic potential of the soil (*Zeta potential*) thus to improve the Mercury desorption from soil matrix; exhausted electrolyte solution will be stored and treated ex situ. Unfortunately, any data about the application work in progress was available; however, thanks to ARPAV database , it could be assumed that the application did not reach the expected results. Similar configuration was tested by USAEC in 2000 , any Mercury remediation was achieved.

7.2.2.3 N_2749 module

In this case the configuration of the ECRT patent was engineered by ECP society and in comparison with the VP_110 several differences may be found. Electrodes were arranged into a circle of 12 m of diameter (field test conducted by the patent owner had demonstrated that higher distances are related to higher energy requirements) where six cathodes were disposed on the circle's boundaries and one anode in the center of the configuration (figure 7.2.2.3.1). Carbon steel electrodes (cathode of 150 mm internal diameter; slotted anode of 170 mm internal diameter) were inserted down to 5 m depth on the ground; any casing was used in order to promote the precipitation of Mercury on the electrode's surface.

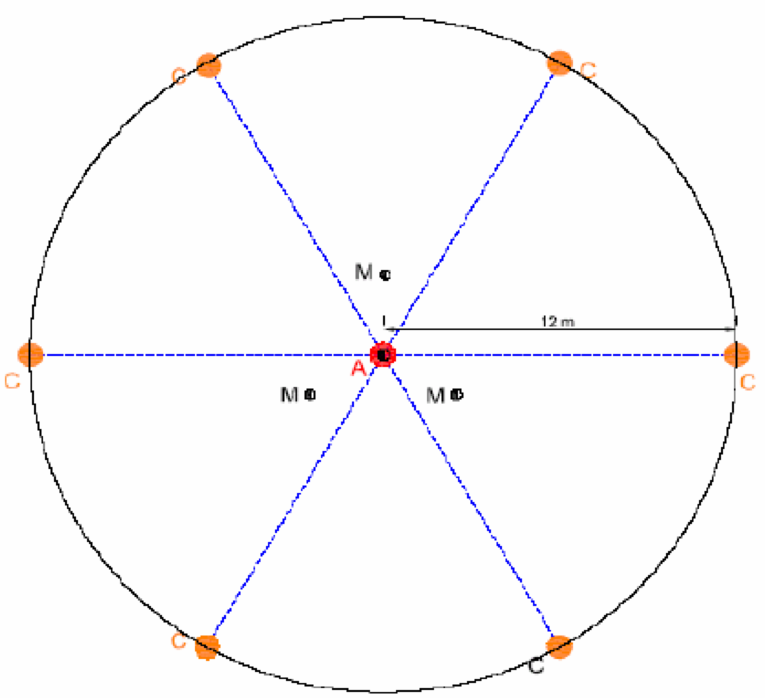


Fig. 7.2.2.3.1 Circular configuration of the N_2749 ECRT application. Source: Progetto definitivo di bonifica dei terreni contaminate con misure di sicurezza area vecchio pertrolchimico, 2008.

It should be pointed out that any electrolyte solution was thought to be used during this application as soil's water was considered to be sufficiently efficient for the Mercury's ions transport; so, humidity of the soil was checked in continuous and kept over 15%-20% water content by the addition of water into anodes and re-watering wells. Similar configuration was tested by EPA.,2007, any Mercury remediation was achieved. The absence of the recirculation system may limit the feasibility of the this application: by inserting electrodes at 5 m depth, interactions between the Mercury-enriched-pore water and the aquifer may arise. A the same time, accumulation of other ions on the electrode's surface may occur due to direct contact of the devices within the soil, thus decreasing the conductivity and efficiency of the application. Unfortunately, any data about the application work in progress was available; however, thanks to ARPAV database , it could be assumed that the application did not reach the expected results.

7.3 Hg speciation: overview

As it has been often said during this critical review, the speciation of the target's pollutants has to be considered of primary importance in order to evaluate the feasibility of the remediation project. During the cloro-soda plant's description a brief description of environmental consequences of Mercury pollution in soil was introduced; on the contrary, in this chapter the focus will concern Mercury geochemical cycle and Mercury speciation in soils.

Mercury is naturally present into ecosystems as the final result of rock's weathering, furthermore, it may be found on deposits under regions characterized by subduction or deep-focus earthquakes (Fitzgerald *et al.,* 2007). However, different forms of oxidation state may exist: Hg^0 metallic Mercury, $Hg_{(I)}$ mercurous and $Hg_{(II)}$ mercuric Mercury. Concerning metallic Mercury, due to its very low melting point (-38,87°C) it is present as a sparkling metallic liquid at ambient temperature; in comparison to other metals it shows an higher specific resistance combined to an elevated vapor pressure. Its high volatile tendency makes Mercury to easily evaporate even at ambient temperature. On the other hand, the comparison between the two ionic species reveals that $Hg_{(I)}$ compounds tends to have a lower solubility and forms ionic bonds; vice versa, $Hg_{(II)}$ compounds tend to form covalent bond and show and higher volatility and solubility. The most remarkable forms of Mercury that maybe found into soil samples and biological matrix had been reported in table 7.3.1 (Morita *et al.,* 1998); at same time it should be underlined that Mercury may form inorganic compounds with great affinity with HS^-, Cl^- or OH^-.

Tab. 7.3.1 Most important species of Mercury in environmental samples. Source: Morita *et al.,* 1998.

Elemental Mercury	**Inorganic Mercury species**	Hg^0
Mercuric ion		Hg^{2+}
Mercurous ion		Hg^+
Mercury sulfide		HgS
MethylMercury	**Organic Mercury species**	CH_3Hg^+
EhtylMercury		$C_2H_5Hg^+$
PhenylMercury		$C_6H_5Hg^+$
DimethylMercury		$(CH_3)_2Hg^+$

It is worthy to be reminded that among the several species of Mercury, Hg^0 and $(CH_3)_2Hg^+$ exhibit great volatility properties while $HgCl_2$ has the greater solubility in water. On the other hand HgS had been found to have volatility and solubility features close to zero thus lending to cinnabar a great stability into the environment. It is commonly accepted that Mercury concentrations in soil are related both to natural causes such as the presence of specific rocks, pH values and soil properties and to local anthropogenic sources of pollution.

However, as previously mentioned, each form of Mercury present in the soil has its own characteristics of toxicity and mobility; following the framework proposed by Han *et al.,* 2003, Mercury's species may be classified according to their mobility as follow:

- Mobile alkyl species: very mobile and toxic compounds formed by organic species of Mercury such as CH_3HgCl, CH_3HgOH or $(CH_3)_2Hg$;

- Inorganic soluble species: such as $HgCl_2$, $HgSO_4$, $Hg(OH)_2$ and other mercuric salts;

- Semi mobile species: such as metallic amalgam of Mercury and mercuric inorganic compounds bonded with sulphur;

- Non mobile species: such as HgS, HgSe that are not susceptible to mobilization.

In parallel, particular attention on the Mercury species classification proposed by Issaro *et al.,* 2009 should be given as reported in table 7.3.2:

Tab. 7.3.2 Mercury species classification. Source: Issaro *et al.,* 2009.

Propierties	**Compound**
Volatile compound	Hg^0; $(CH_3)_2Hg$.
Reactive species	Hg^{2+}; HgX_2; HgX_3^-; HgX_4^{2-} with X=OH^-, Cl^- and Br^-; HgO on aerosol particles; Hg^{2+}complexes with organic acids; methylMercury CH_3Hg^+; CH_3HgCl; CH_3HgOH.
Non-reactive species	$Hg(CN)_2$; HgS; Hg^{2+} bounded to S atoms in humic matter.

Interactions between these different species may be summarized into a set of geochemical processes that involves atmosphere, hydrosphere and geosphere as well. The first step of the geochemical cycle of Mercury could be seen as the volatilization from soils, water or punctual sources to the atmosphere; Fitzegerald *et al.,* 2007 suggest that almost the 95% of the total Mercury amount exist as elemental Mercury dissolved in the atmosphere in combination with particulate forms of Hg^{2+}. It has been estimated that residence time of elemental Mercury in the atmosphere is closed to one year; during this period oxidation and adsorption reactions may occur thus to force its deposition on the soil. Wash out by rainfalls seems to be the most influencing pathway for atmospheric Mercury removal; on the other hand, dry deposition had been demonstrated to be a significant route for Mercury removal from the atmosphere. Figure 7.3.1 represents a graphical summary of atmospheric chemical and physical reaction of Mercury.

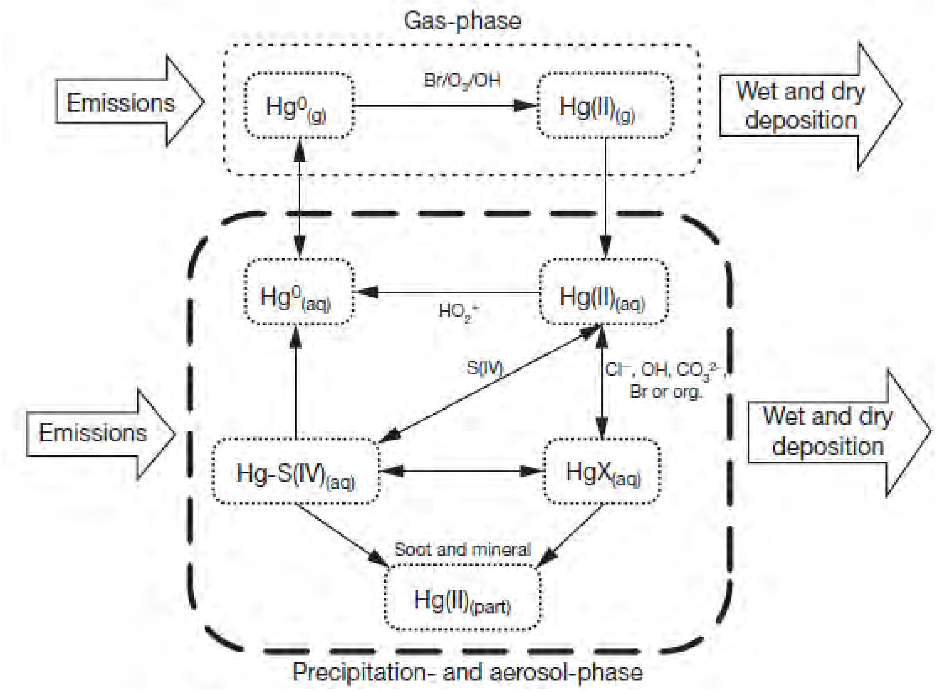


Fig. 7.3.1 Most important transformations of Mercury in atmosphere. Source: Fitzgerald *et al.,* 2007.

As it could be easily guessed, targets of wet and dry atmospheric depositions are water surfaces and soils; in both cases Mercury undergoes to a series of reactions that modify its fate into the environment; the mixture of soil, water, air and microorganism‘s presence has a role of primary importance. Concerning transformations in soils, known the great affinity of Mercury species with compounds composed by sulphur, it could be stated that main reactions involves adsorption to organic matter and solubilization on ground water. As it had been studied by Palmieri *et al.,* 2006, the distribution of Mercury in soil matrix depends on several parameters such as: pH, soil grain size and dissolved ions. It had been proved that Mercury tend to accumulate on clayey fraction of the soil as a function of the cation exchange capacity propierties. In parallel, reactions of oxidation transforms the $Hg_{(I)}$ into mercuric forms $Hg_{(II)}$ that is usually found at higher concentrations in soil. At the same time, mercuric cations tend to form very soluble inorganic compounds with Cl^- or insoluble HgS. As it has been previously mentioned, in addition to chemical and physical reactions, Mercury compounds are susceptible to biological transformations too; in particular, methylation is a process of great concern. What is likely to happen during methylation is the exchange, performed by specific sulfate-reducing bacteria, of a ionic $Hg_{(II)}$ with a methyl group ($-CH_3$); in such way stable inorganic species are converted into more mobile and toxic organic fractions of Mercury. This transformation let the organic metal compound to be lipophilic and able to bioaccumulate on trophic chain. Essential conditions suitable for methylation processes are related to anoxic regime and organic matter abundance, furthermore, water is required by the biological process. So, as reported by Bloom *et al.,* 2003, saturated sediments of ponds and lagoons are considered to be the best conditions for methylation; on the other hand, also marine and sandy sediments had been proved to support these reaction but with slower kinetics. It should be underlined that, in combination with methylation reactions also demethylation reactions occur; but, while methylation is essentially driven by biotic processes, demethylation could be performed both by biotic and abiotic pathways. As it had been mentioned by Davis *et al.,* 1997, methyl-Mercury distribution on the soil column tends to be directly proportional to the organic matter content and temperature, while seems to be inversely proportional to pH and sulphates concentrations. A schematic summary of the most relevant reactions occurring in aquatic environment is reported in figure 7.3.2.

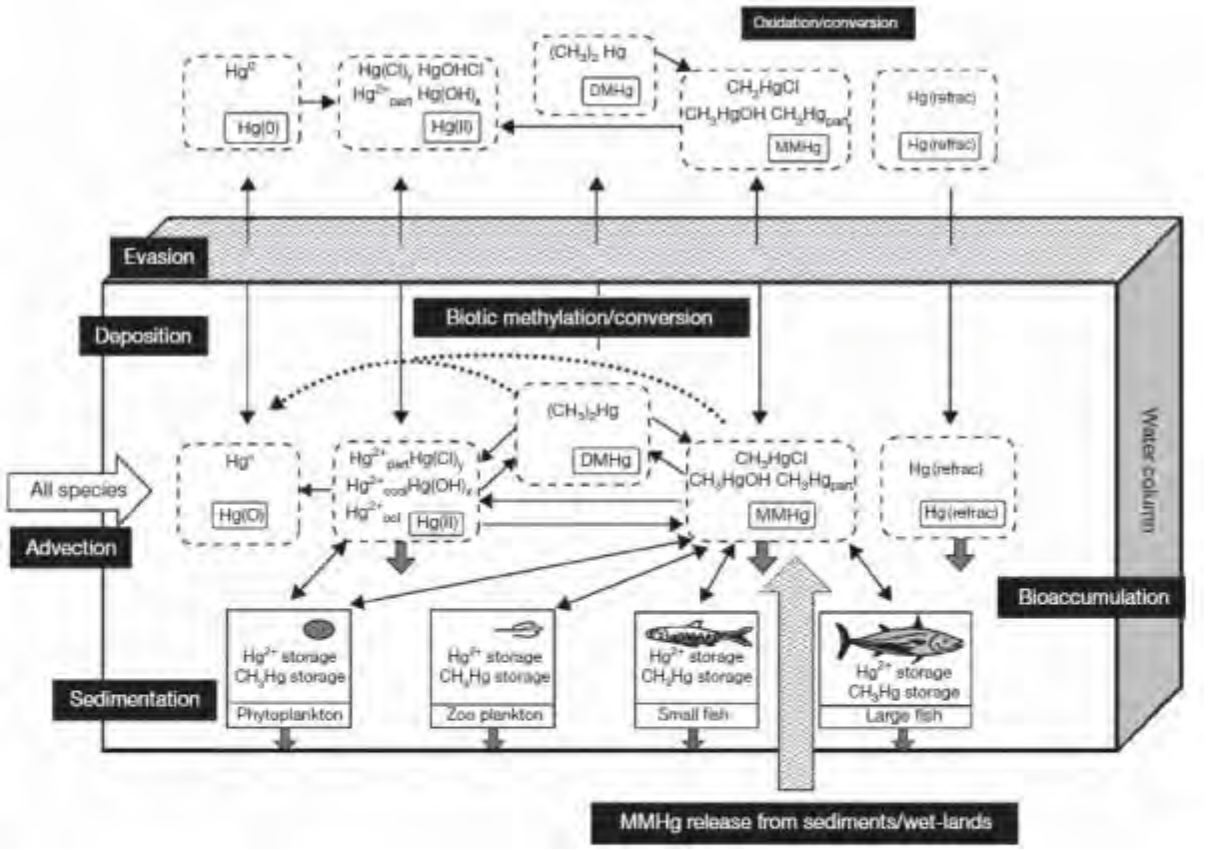


Fig. 7.3.2 Most important transformations of Mercury in aquatic environment. Source: Fitzgerald *et al.,* 2007.

7.4 Hg speciation: Total Mercury assessment

As it had been previously discussed, while evaluating the risk assessment of a polluted site, total Mercury could be considered as a meaningless value due to the fact that any information about the mobility of its fraction may be assessed (Issaro *et al.,* 2009; Wang *et al.,* 2012). Anyhow, as it will be evident in the next chapter, total Mercury measurements are always performed as it represents a robust and reliable data often based on standard and certified methods. Hundreds of paper had been published for the determination of total Mercury into different environmental and biological samples (Morita *et al.,* 1998); methods such as Chemical Vapor Generation (CVG) (Gao *et al.*,2012), Atomic Adsorption Spectroscopy (AAS) (Reis *et al.*,2015), extraction with aqua regia (Boszke *et al.,* 2008), Atomic Emission Spectrometry (AES) (Wu *et* al.,2012) had been validated. In order to better understand results obtained in next chapters, methods that had been used during the speciation analysis of the bench scale, of 2014 speciation and 2015 speciation will be presented in details in this paragraph.

7.4.1 EPA 6010/07

This standardized method had been used both at ARPAV laboratories during the cross-sample examination and at R&C lab during the total Mercury assessment. It is based on the combination between acid digestion with aqua regia and a further ICP device spectrum analysis; detection limits of the method are fixed at 1 mg/kg of Hg. Weighing of the specimen is performed into two steps: the first concern the soil sample after the 4 ^{o}C storage, the second is proceeded by the drying of the sample at 40 ^{o}C for 48 hours; after the homogenization at 2 mm, soil sample is dried at 105 ^{o}C in order to assess the residue humidity. Specimen that undergoes to mineralization is composed by 1 gr of the above mentioned sample (2mm-105 ^{o}C) while the aqua regia solution is obtained by the combination of 2ml of H_2O, 2.5 ml of HNO_3 and 7.5ml of HCl; the specimen is further heated at 120 ^{o}C for 15 minutes. The solution is filtered at 0.45 µm and transferred into a 15 ml probe. After the calibration of the ICP device, the liquid sample is analyzed by the software. It should be pointed out that both chemical and physical interferences may affect the spectrum evaluation; however, EPA 6010C is widely recognized to be a reliable and robust method.

7.4.2 EPA 7473

The following procedure had been used during the lab scale ECRT feasibility study performed at the University of Ferrara; it relies on the sequence use of a controlled heating of the sample in an oxygenated decomposition furnace, amalgamation of decomposed products and final analysis into an atomic absorption spectrophotometer. The instrument detection limit for this method is

0.01 ng of total mercury and it could be applied on both solid and aqueous samples; standardized soil samples are composed with 0,5 gr of solid material. The sample is dried and thermally decomposed (750 ^{o}C) in an oxygen environment, releasing mercury vapor. The mercury vapor is transported by oxygen over the amalgamator that traps the mercury. Once the sample is completely decomposed the trapped mercury is desorbed rapidly by heating the amalgamator; the mercury vapor passes through two absorbance cuvettes. The flow path through the spectrometer and cuvettes is maintained at approximately 120 ^{o}C, by a heating unit. The detector is connected to a computer for data acquisition and analysis.

7.4.3 R&C aqua regia extraction and ICP analysis procedure

The following procedure (proposed by the University of Ferrara) had been used in order to assess the total Mercury concentration during the speciation analysis conducted by R&C lab; it should be reminded that the method is still being validated. Similarly to EPA 6010 C, total Mercury evaluation is performed by the combination of an acid digestion and the further ICP analysis but few differences were adopted. It was preferred to avoid both heating and sieving of the soil during the sample preparation in order to prevent any losses of Hg^0; so, drying of the soil was obtained by a freeze-drying procedure. In parallel, as it could be seen in figure 7.4.3.1, in order to homogenize the specimen, a milling stage had been introduced on the bulk soil sample. Specimens were composed by 0.5 gr of the soil sieved at 0.25 mm and mixed up with 5 ml of aqua regia (1.5 ml of HNO_3 and 4.5 ml of HCl), the mineralization were obtained by heating the sample at 180 ^{o}C for 1.5 h. After the cooling of the specimen, a fitting quantity of deionized water is added to the sample to obtain 25 ml of solution that is analyzed into the ICP device.

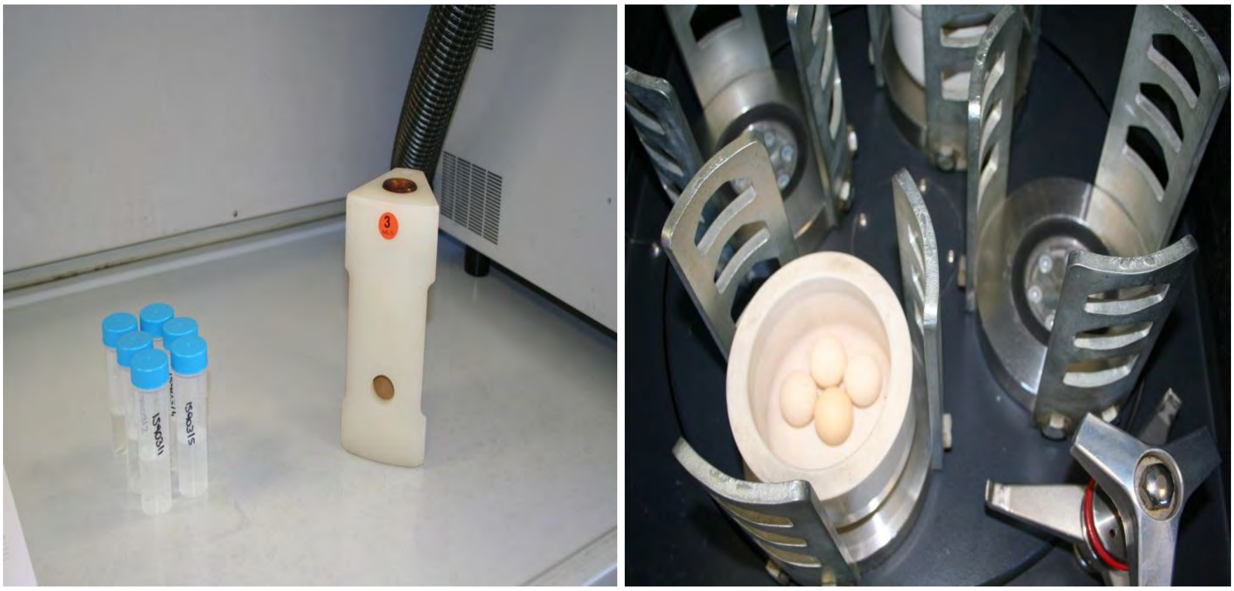


Fig. 7.4.3.1 Specimen preparation and aqua regia extraction.

7.5 Hg speciation: techniques

As it could be found in literature, hundreds of studies had been developed on Mercury speciation but an unique solution seems far to be found (Wang *et al.,* 2012); at the same time, among the several analytical method for Mercury assessment and its speciation that had been proposed, a similar framework seems to be repeated (Issaro *et al.,* 2009). During speciation analysis, extraction, quantification and concentration steps are commonly found. More precisely, speciation analysis may be performed in order to evaluate total Mercury concentrations, specific species presence or the sequential evaluation of all the species present in the sample. As it had been reported by different authors, during Mercury speciation the extraction step is still matter of scientific controversy due to its great variety of methods and applications; single or sequential extraction, distillation, thermal extraction and pyrolysis are common used techniques. A brief summary of the techniques used during the speciation analysis on VP_38 soil sample will be given in the following chapter.

7.5.1 Sequential extraction

Sequential extraction speciation is based on the use of different reagents with an increasing extractability power in order to assess the mobility of elements from different compartments (Issaro *et al.,* 2009). Common used reagents are strong acids that are able to separate Mercury from other elements and get it into solution; as it could be easily guessed, these reagents must be more element-specific as possible thus to get into solution just the target element. Still nowadays the specificity of reagents is seen as a limitation of these technique (Kim *et al.,* 2003). Furthermore, as it had been reported by Issaro *et al* (2009), transformations, losses and alteration of Mercury species may affect the sequential extraction. Different kind of sequential extraction method had been validated (table 7.5.1.1); more precisely, several extractants had been tested through the years but a general framework could be described as follow (Issaro *et al.,* 2009):

1. *Deionized water:* used to extract the water soluble fraction of Mercury;

2. NH_4Ac, NH_4Cl, $MgCl_2$, $CaCl_2$, $NaNO_3$: reagents used in order to separate Mercury by ion-exchange pathways; fraction collected is defined as exchangeable.

3. $NaOH$, H_2O_2, KOH: oxidizing reagents used for extracting Mercury from the organic matter;

4. *Aqua regia,* HNO_3, $K_2S_2O_8$: reagents with high acidity used for the dissolution of the strongest bonds between Mercury and the soil sample.

Tab.7.5.1 Reactants used for Mercury speciation in soils and/or sediments. Source: Issaro *et al.,* 2009.

Author	**Reagents**	**Compound extracted**
Renneberg and Dudas (2001)	Deionized water	Water soluble
	1M $MgCl_2$	Exchangeable compounds
	0.2M NaOH	Organic acids I bound Mercury
	0.005M NaOH	Organic acids II boundMercury
	0.005M CH_3COOH	Organic basic
	3% H_2O_2 (pH 2)	Residual organic matter
	30% H_2O_2 (pH 2)	Residual organic matter
	$HNO_3/K_2S_2O_8$	Residual
Biester and Scholz (1997), Di Giulio andRyan (1987)	Deionized water	Water soluble
	1M NH_4Ac	Exchangeable compounds
	1M NH_4OH	Fulvic and humic
	0.02M HNO_3/30% H_2O_2/1M NH_4Ac	Organic sulfur
	Aqua regia	Residual
Bloom *et al*. (2003), Bloom and Katon (2000)	Deionized water	Water soluble
	HCl/CH_3COOH	Human stomach acid soluble
	KOH	Humic
	HNO_3	Complex-compounds
	Aqua regia	Residual and HgS
	$HF/HNO_3/HCl$	(if bauxite and hematite exist)
Neculita *et al*.(2005)	Deionized water	Water soluble
	0.5M NH_4Ac-EDTA+ $CaCl_2$	Exchangeable compounds
	0.2M NaOH+ CH_3COOH (4% v/v)	Residual compounds
	HNO_3 +H_2SO_4 + $HClO_4$	Organic compounds
Wang *et al*.(2003)	0.1M $CaCl_2$ (pH 7)	soluble Hg and exchangeable Hg
	1M HCl + 1% $CuSO_4$	HCl-dissoluble Hg
	1% KOH	Organic bound Hg
	2M HNO_3	Hg^0 form
	Aqua regia	Residual Hg
Wallschlager *et al*. (1998)	Deionized water	Water soluble
	0.01M HNO_3 (pH 2)	Organic extracted/acid
	1M KOH	Organic extracted/base
	Na_2S	Residual
	Concentrated HNO_3	HgS
Wang *et al*.(1997)	1M $CaCl_2$	Available Hg
	HCl/0.1M $KBrO_3$-KBr	Hg bound to organic matter
	$H_2SO_4/HNO_3/KMnO_4$	Residual Hg
Miller *et al*.(1995)	0.01M K_2SO_4 + 0.01M KCl, Toluene	Organic and soluble compounds
	0.2M HNO_3	Acid soluble
	1:3 HNO_3 +H2O	HNO3 soluble
	1:6:17 HCl +HNO_3 +H_2O	Residual

Sakamoto *et al.* (1992)	$CHCl_3$ H_2SO_4 $CuCl_2/HCl$ (3%NaCl) HgT – extracted-Hg in all fractions above	Organic Mercury HgO HgS Residual

Boszke's sequential extraction method (Boszke *et al.,* 2008) was chosen to be performed during the speciation on the bench scale application at the University of Ferrara; key steps and the categories founded may be summarized as follow (data referred to 5 gr of contaminated soil):

1. *Chloroform extraction:* the soil specimen pass through four mechanical treatment that comprehends shaking (3 hours, mixed with 30 ml of chloroform), centrifugation (15 minutes, at 3,000 rpm), filtration (on a 0.45 µm diameter cellulose acetate filter); these three steps are repeated with the addition of 30 ml of chloroform. A further extraction (3 minutes) with 10 ml of 0.1 M $Na_2S_2O_3$ is performed to obtain the *F1 class: organoMercury species*.

2. *Deionized water extraction:* consequently, the soil sample is shaken for 3 hours with 30 ml of deionized water, centrifuged for 15 minutes at 3,000 rpm and finally filtrated on a 0.45 µm diameter cellulose acetate filter. From this step *the F2 class: water soluble species* is obtained.

3. *Hydrochloric acid extraction:* after 1 hour of shaking stage with 25 ml of 0.5 M HCl solution, centrifugation and filtration are developed like in the previous steps. *F3 class: acid soluble species* is assessed.

4. *Sodium hydroxide extraction: F4 class: associated with humic matter* is quantified by shaking the soil sample with 30 ml of 0.2 M NaOH solution for 1 hour and by centrifugation and filtration steps.

5. *Aqua regia (D1) extraction:* soil sample is digested with 12 ml of 37% HCl and 4 ml of 65% HNO_3 to obtain *D1 fraction.* More precisely, *F5 class: elemental Mercury* is estimated as the difference between *D1* and *D2 fractions*.

6. *Aqua regia (D2) extraction:* after the sodium hydroxide extraction step, the specimen is heated for 6 hours at 150°C and then digested with 12 ml of 37% HCl and 4 ml of 65% HNO_3. *F6 class: residual (HgS)* was obtained.

A graphical summary of the procedure is presented in Figure 7.5.1.

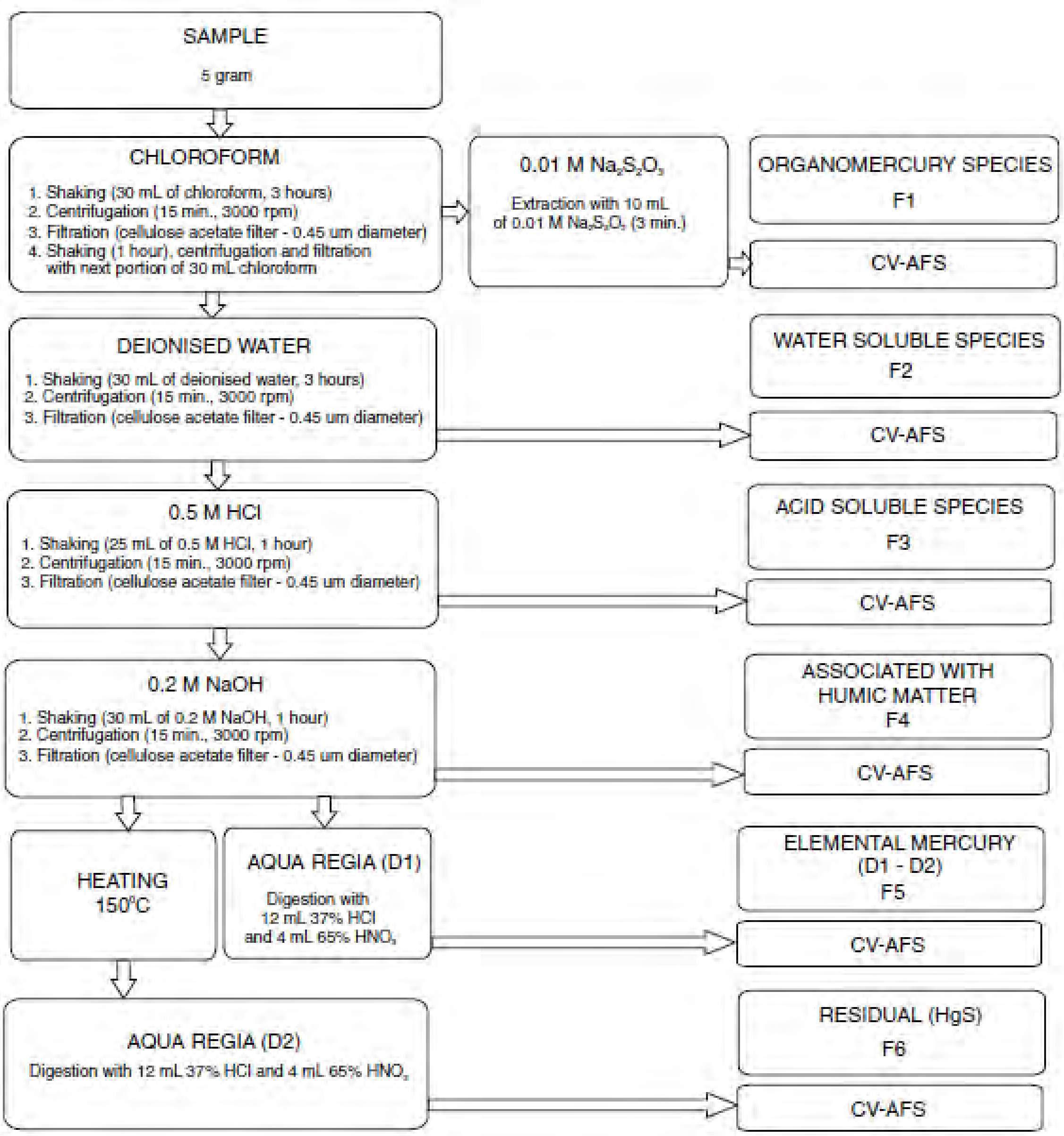


Fig. 7.5.1 Graphical summary of Boszke's sequential extraction method. Source: Boszke *et al.*, 2008.

It should be pointed out that, after the extraction of the target fraction, Mercury concentrations were determined by Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS) at the end of each step. Consequently the Total Mercury concentration was calculated as the sum of the different fractions obtained by speciation and compared to validated and reliable method.

7.5.2 Acid extraction and thermo desorption combination method

The procedures proposed by Babko *et al.,* 2001 and Boszke *et al.,* 2008 quantified the Hg^0 concentration throughout indirect measures related to the other fractions concentrations obtained during the speciation; in this way, as it could be easily guessed, the default imprecision of the device that affect the direct measurement of the other species may led to huge mistakes on the metallic Mercury evaluation. In order to reduce this lack of precision, that seemed to affect in particular low-concentrated samples, a new procedure was proposed by the University of Ferrara and used by R&C lab during this study. It should be underlined that details of the procedure had been omitted due to the fact that method's validation is still matter of study and the technique is going to be published soon. However in this chapter will be reported a brief summary of what was done during the laboratory experience of March 2015.

The following method combines the reliability of aqua regia extraction and ICP analysis with a new approach on thermodesorption and GC/MS mercury analysis. More precisely, specimen preparation were obtained by drying at low temperature the soil sample and then milling it at a fixed dimension in order to homogenize the soil fraction. During the analysis two extractions were performed and in particular: extraction with aqua regia, following the procedure described in paragraph 7.4.3, in order to assess the total Mercury concentration, extraction with water in order to assess the water-soluble fraction of total Mercury (e.g. $HgCl_2$). Concerning water extraction (figure 7.4.3.1), it was performed by a leaching test were water-shaking, filtration and ICP analysis (figure 7.4.3. 1) steps were performed on 5 g of milled sample.

Fig. 7.5.2.1 Water leaching test and ICP analysis.

On the other hand, thermo-desorption analysis by GC/MS device were performed in order to quantify the volatile fractions of Mercury (figure 7.5.2.2). The organic fraction of Mercury, that was considered to be represented by Methyl-Mercury chloride, Ethyl-Mercury chloride and Byphenil-Mercury, had been evaluated by direct thermodesorption of 0.15-0.30 gr of milled soil sample mixed with 1µl of BFB standard solution; validation of the device had been performed on two standard solution into a five step incremental procedure. Concerning the metallic Mercury assessment, it was performed by the direct thermodesorption of 0.15 gr of milled soil sample mixed with 1µl of BFB standard solution; while validation had consisted on the evaluation of 5 standard solutions composed by increasing concentrations of $NaBH_4$, NaOH and Hg^{2+} missed with 1µl of BFB standard solution.

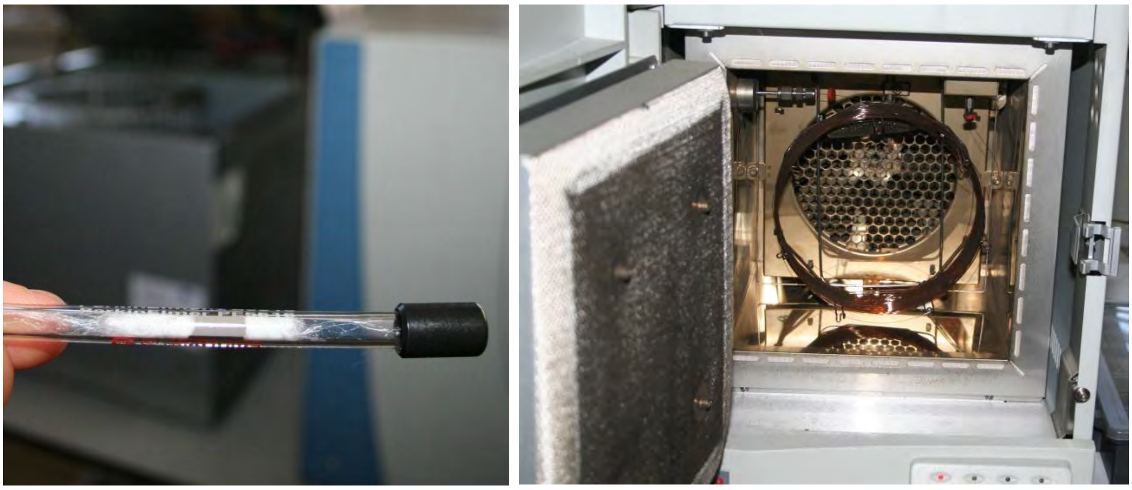


Fig. 7.5.2.2 Thermodesorption soil specimen and GC/MS device.

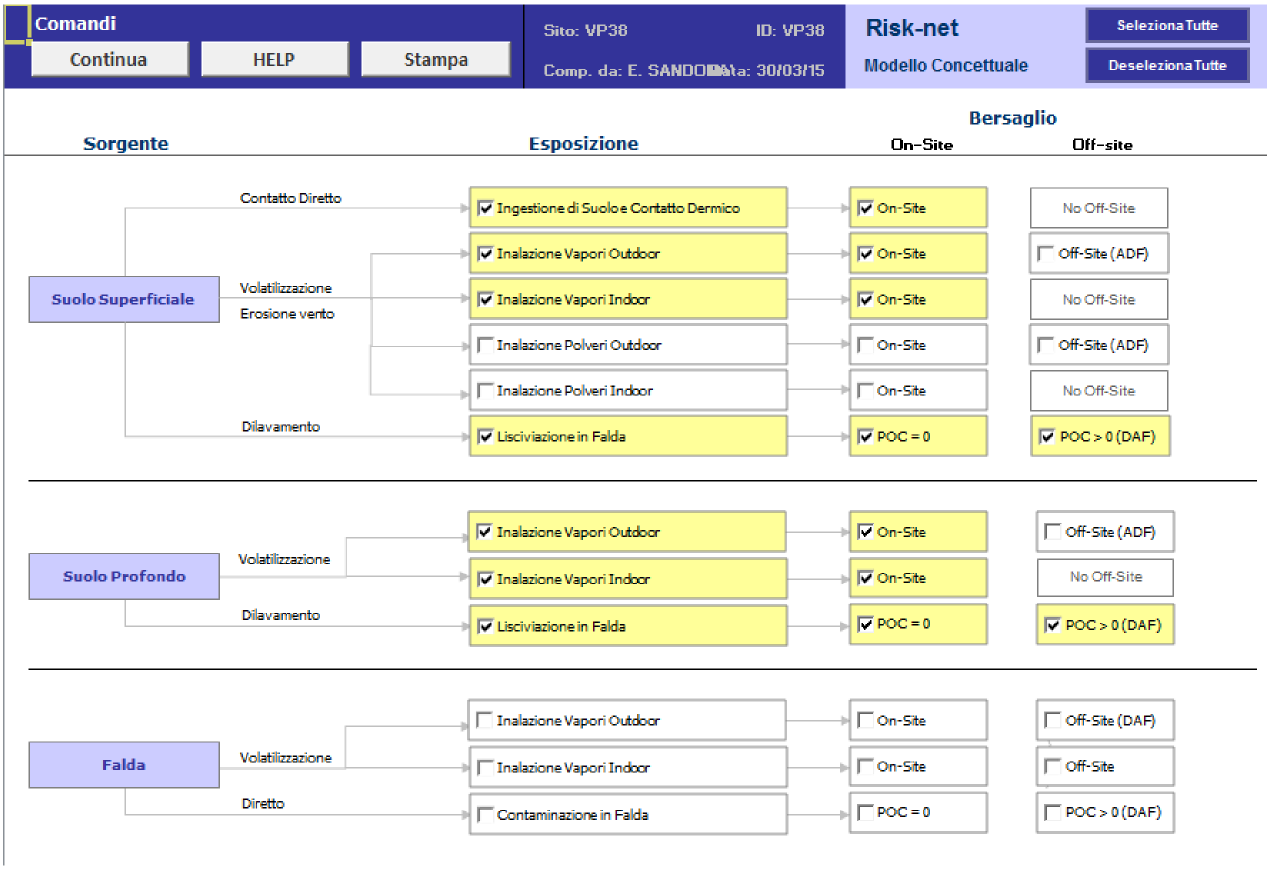
The evaluation of the so called ‗‗residual Mercury fractions‘‘, had been slightly modified in comparison with other speciation methods; more precisely, this fraction was considered to be split into Calomel and Cinnabar thus giving a more precise results of the kind of stable Mercury form. After the Hg^0 release obtained by the saturation of the soil sample with an acid solution, quantification of Calomel had been evaluated by thermodesorption; consequently, Cinnabar concentration was analytically calculated as the difference between total Mercury and the summation of the other fractions. Following this method it was possible to obtain the concentrations of the following Mercury fractions:

- Total Mercury extractable in aqua regia;
- Water soluble Mercury;
- Organic forms of Mercury: methyl-Mercury chloride, ethyl-Mercury chloride and diphenyl-Mercury;
- Residual forms: Calomel and Cinnabar.

7.6 Risk analysis

It should be pointed out that the following risk analysis could not be expected to be an exhaustive research due to the lack of informations about the site's characteristics and due to the fact that risk assessment is not the main argument of this thesis. However, in order to validate the hypothesis that had been proposed in the previous paragraph, a quick risk assessment had been performed; more precisely, as a function of the input data (that were divided into Total_Hg and Speciation_Hg series) two calculations were performed.

Risknet 1.0 and Risknet 2.0 risk assessment software were both used during the simulation thanks to their wide database that includes all the contaminants prescribed by the Italian law and the recent introduction of validated data about the different species of Mercury. As it could be seen from the conceptual model represented in figure 7.6.1, pathways of risk were considered to be related to inhalation, direct ingestion, dermal contact and leaching from soil to groundwater just on the unsaturated portion of the soil. Inhalation of dusts was neglected due to the presence of grass on site.



Suolo Superficiale
- ☑ Ingestione di Suolo e Contatto Dermico – ☑ On-Site – No Off-Site
- ☑ Inalazione Vapori Outdoor – ☑ On-Site – ☐ Off-Site (ADF)
- ☑ Inalazione Vapori Indoor – ☑ On-Site – No Off-Site
- ☐ Inalazione Polveri Outdoor – ☐ On-Site – ☐ Off-Site (ADF)
- ☐ Inalazione Polveri Indoor – ☐ On-Site – No Off-Site
- ☑ Lisciviazione in Falda – ☑ POC = 0 – ☑ POC > 0 (DAF)

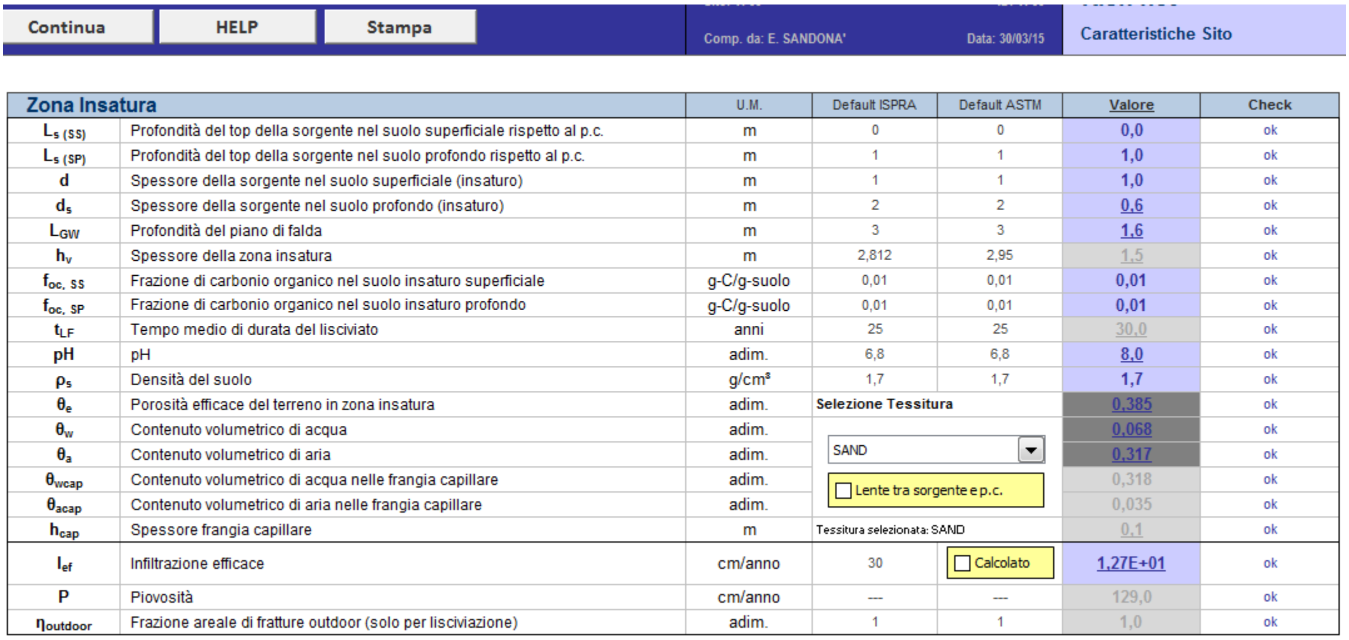
Suolo Profondo
- ☑ Inalazione Vapori Outdoor – ☑ On-Site – ☐ Off-Site (ADF)
- ☑ Inalazione Vapori Indoor – ☑ On-Site – No Off-Site
- ☑ Lisciviazione in Falda – ☑ POC = 0 – ☑ POC > 0 (DAF)

Falda
- ☐ Inalazione Vapori Outdoor – ☐ On-Site – ☐ Off-Site (DAF)
- ☐ Inalazione Vapori Indoor – ☐ On-Site – ☐ Off-Site
- ☐ Contaminazione in Falda – ☐ POC = 0 – ☐ POC > 0 (DAF)

Fig. 7.6.1 Active pathways of transport considered during the risk assessment (Risknet 2.0).

Furthermore, the software indicates the distinction between superficial and deep soil that are respectively confined at 0-1m depth and 1-1.5m depth; both on-site and off-site scenario were considered for the run off to the groundwater media. Unfortunately, the groundwater characterization and the related risk evaluation were not available for the VP38 area. The receptors of the risk were identified as adult workers that may be present both in outdoor ambient and indoor ambient; exposure parameters for human targets were assigned by default database that had been proposed by ISPRA. On the other hand, the target for the exposure pathway –soil leaching to groundwater", as the Italian law requires (D.Lgs. 152/2006), are the groundwater concentration limits at the border of the site.

Concerning the site characterization, it was assumed that the VP_38 area may be approximated to a closer site which data were available; this hypothesis may greatly affect the veracity of the simulation due to the high heterogeneity of soil composition in Porto Marghera. However, it was considered to combine the worst theoretical characteristics of soil's composition (sand) with the real features of the soil that were assessed on site; an example of the soil's characterization sheet is represented in figure 7.6.2.



Comp. da: E. SANDONA'

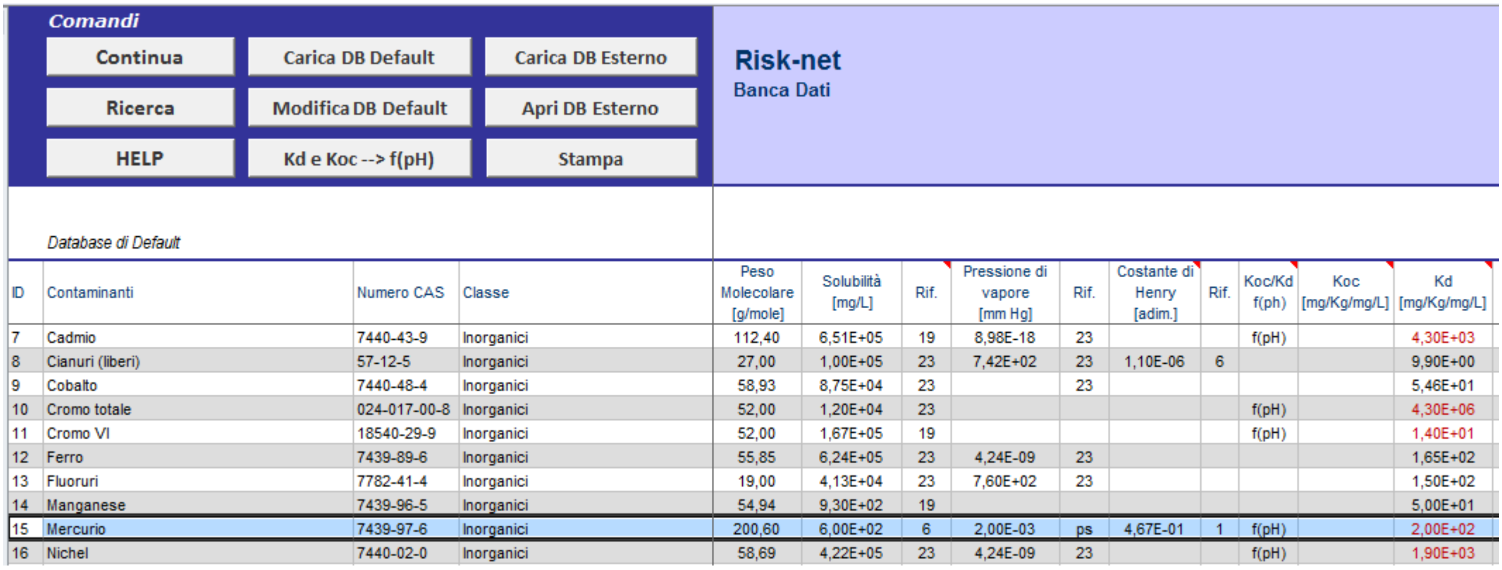
Data: 30/03/15

Caratteristiche Sito

Zona Insatura		U.M.	Default ISPRA	Default ASTM	Valore	Check
$L_{s\ (SS)}$	Profondità del top della sorgente nel suolo superficiale rispetto al p.c.	m	0	0	0,0	ok
$L_{s\ (SP)}$	Profondità del top della sorgente nel suolo profondo rispetto al p.c.	m	1	1	1,0	ok
d	Spessore della sorgente nel suolo superficiale (insaturo)	m	1	1	1,0	ok
d_s	Spessore della sorgente nel suolo profondo (insaturo)	m	2	2	0,6	ok
L_{GW}	Profondità del piano di falda	m	3	3	1,6	ok
h_v	Spessore della zona insatura	m	2,812	2,95	1,5	ok
$f_{oc,\ SS}$	Frazione di carbonio organico nel suolo insaturo superficiale	g-C/g-suolo	0,01	0,01	0,01	ok
$f_{oc,\ SP}$	Frazione di carbonio organico nel suolo insaturo profondo	g-C/g-suolo	0,01	0,01	0,01	ok
t_{LF}	Tempo medio di durata del lisciviato	anni	25	25	30,0	ok
pH	pH	adim.	6,8	6,8	8,0	ok
ρ_s	Densità del suolo	g/cm³	1,7	1,7	1,7	ok
θ_e	Porosità efficace del terreno in zona insatura	adim.	**Selezione Tessitura**		0,385	ok
θ_w	Contenuto volumetrico di acqua	adim.			0,068	ok
θ_a	Contenuto volumetrico di aria	adim.	SAND ▼		0,317	ok
θ_{wcap}	Contenuto volumetrico di acqua nelle frangia capillare	adim.	☐ Lente tra sorgente e p.c.		0,318	ok
θ_{acap}	Contenuto volumetrico di aria nelle frangia capillare	adim.			0,035	ok
h_{cap}	Spessore frangia capillare	m	Tessitura selezionata: SAND		0,1	ok
I_{ef}	Infiltrazione efficace	cm/anno	30	☐ Calcolato	1,27E+01	ok
P	Piovosità	cm/anno	---	---	129,0	ok
$\eta_{outdoor}$	Frazione areale di fratture outdoor (solo per lisciviazione)	adim.	1	1	1,0	ok

Fig. 7.6.2. Example of the soil's characterization input data (Risknet 2.0).

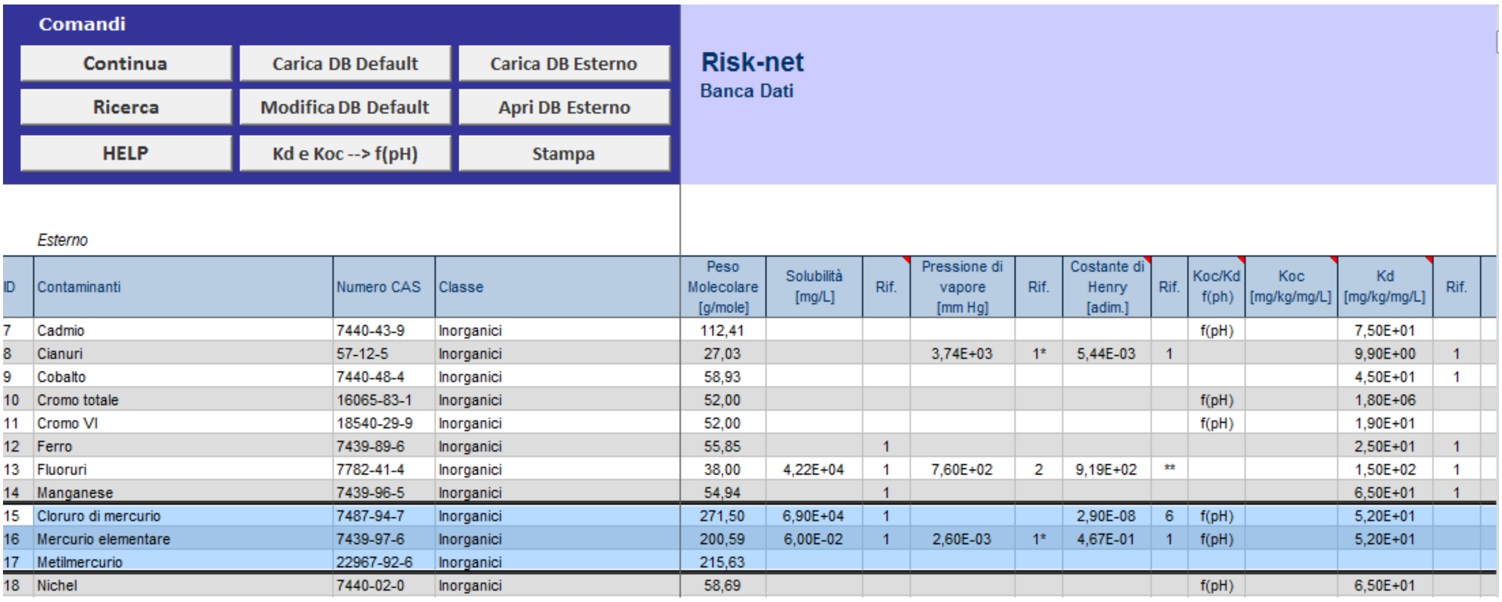
As it had previously mentioned, two different dataset of contaminants were used during the risk assessment: in the former (figure 7.6.3), considering the features that were given by the software 2012 database (Risknet 1.0), input characteristics of the contaminant were supposed to be related just to total Mercury; on the contrary, in the latter case (figure 7.6.4) it was considered that the characteristics of the contaminant were related to the species that were found during the speciation analysis and the related 2015 database values (Risknet 2.0). The concentrations of trenches number 4A and 9B were chosen as input concentrations thanks to their high absolute value and fractionation. Due to the lack of toxicological information about Biphenyl-Mercury, it was assumed the presence of Methyl-Mercury (a well-known toxic) with the same concentration of Biphenyl-Mercury. It was a prudent approach because the concentrations of Methyl-Mercury were found to be lower than the detection limit. At the same time, k_d values of Metallic Mercury and Methyl-Mercury were modified with more realistic data that were proposed by EPA (Allison *et al.*,2005).



Database di Default

ID	Contaminanti	Numero CAS	Classe	Peso Molecolare [g/mole]	Solubilità [mg/L]	Rif.	Pressione di vapore [mm Hg]	Rif.	Costante di Henry [adim.]	Rif.	Koc/Kd f(ph)	Koc [mg/Kg/mg/L]	Kd [mg/Kg/mg/L]
7	Cadmio	7440-43-9	Inorganici	112,40	6,51E+05	19	8,98E-18	23			f(pH)		4,30E+03
8	Cianuri (liberi)	57-12-5	Inorganici	27,00	1,00E+05	23	7,42E+02	23	1,10E-06	6			9,90E+00
9	Cobalto	7440-48-4	Inorganici	58,93	8,75E+04	23		23					5,46E+01
10	Cromo totale	024-017-00-8	Inorganici	52,00	1,20E+04	23					f(pH)		4,30E+06
11	Cromo VI	18540-29-9	Inorganici	52,00	1,67E+05	19					f(pH)		1,40E+01
12	Ferro	7439-89-6	Inorganici	55,85	6,24E+05	23	4,24E-09	23					1,65E+02
13	Fluoruri	7782-41-4	Inorganici	19,00	4,13E+04	23	7,60E+02	23					1,50E+02
14	Manganese	7439-96-5	Inorganici	54,94	9,30E+02	19							5,00E+01
15	Mercurio	7439-97-6	Inorganici	200,60	6,00E+02	6	2,00E-03	ps	4,67E-01	1	f(pH)		2,00E+02
16	Nichel	7440-02-0	Inorganici	58,69	4,22E+05	23	4,24E-09	23			f(pH)		1,90E+03

Fig. 7.6.3. Total_Hg input data (Risknet 1.0).



Esterno

ID	Contaminanti	Numero CAS	Classe	Peso Molecolare [g/mole]	Solubilità [mg/L]	Rif.	Pressione di vapore [mm Hg]	Rif.	Costante di Henry [adim.]	Rif.	Koc/Kd f(ph)	Koc [mg/kg/mg/L]	Kd [mg/kg/mg/L]	Rif.
7	Cadmio	7440-43-9	Inorganici	112,41							f(pH)		7,50E+01	
8	Cianuri	57-12-5	Inorganici	27,03			3,74E+03	1*	5,44E-03	1			9,90E+00	1
9	Cobalto	7440-48-4	Inorganici	58,93									4,50E+01	1
10	Cromo totale	16065-83-1	Inorganici	52,00							f(pH)		1,80E+06	
11	Cromo VI	18540-29-9	Inorganici	52,00							f(pH)		1,90E+01	
12	Ferro	7439-89-6	Inorganici	55,85		1							2,50E+01	1
13	Fluoruri	7782-41-4	Inorganici	38,00	4,22E+04	1	7,60E+02	2	9,19E+02	**			1,50E+02	1
14	Manganese	7439-96-5	Inorganici	54,94		1							6,50E+01	1
15	Cloruro di mercurio	7487-94-7	Inorganici	271,50	6,90E+04	1			2,90E-08	6	f(pH)		5,20E+01	
16	Mercurio elementare	7439-97-6	Inorganici	200,59	6,00E-02	1	2,60E-03	1*	4,67E-01	1	f(pH)		5,20E+01	
17	Metilmercurio	22967-92-6	Inorganici	215,63										
18	Nichel	7440-02-0	Inorganici	58,69							f(pH)		6,50E+01	

Fig. 7.6.4. Speciation_Hg input data (Risknet 1.0).

PART 3: RESULTS AND DISCUSSION

7.7 Speciation campaigns

As it had been previously mentioned, speciation analysis were conducted on soil samples taken from the site in order to assess the kind of pollution and the feasibility of the remediation; sampling and speciation were performed in July of 2014 and February of 2015. Considerations and results about filed and lab experiences will be presented in this chapter.

7.7.1 July 2014 speciation campaign

As it could be seen on figure 7.7.1.1, the area that was planned to be treated by ECRT was divided into 10 sampling trenches around the VP_38 piezometer; soil samples for each trench had been divided into two different aliquots at 0-1 m depth and 1-1.6 m depth. The position of sampling points was fixed by considering the middle point of each square of a 5x5 m length network. It should be reminded that Mercury concentrations above the law limits were researched just on the unsaturated portion of soil.

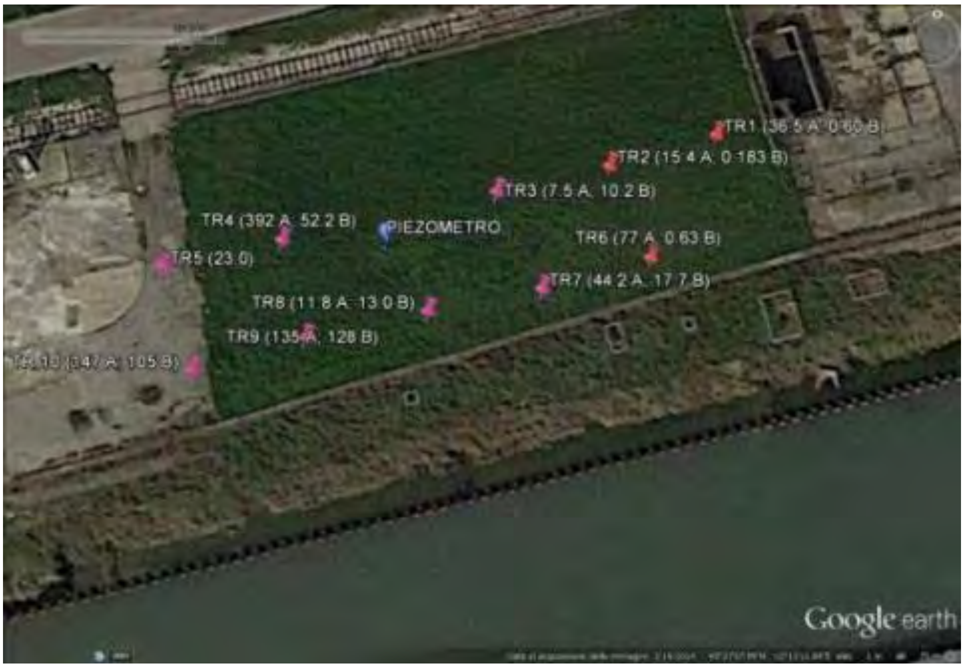


Fig. 7.7.1.1. Planar view of the area and sampling trenches.

Going into details, during the soil sampling DGRV 2922/03 standardized procedure had been followed as prescribed by the above mentioned Agreement program. Trenches were dig by the use of an excavator down to 1 m depth from the ground level, the excavated soil was put aside on the ground (figure 7.7.1.2) and classified as A soil; during the whole procedure, volatile Mercury compounds were monitored by a Jerome mercury-vapor analyzer (any traces of volatile Mercury was detected). In order to collect soil samples from -1 to -1.6m depth the trench was dig again and the excavated soil was put aside (B soil samples).

The soil sampling used in figure 7.7.1.3 was adopted just in one trench in order to assess geotechnical properties of the unsaturated media; in order to avoid any spreading of the pollution in the aquifer any fluid was used during both the insertion of the punch and the soil sample extrusion. In parallel, probing was not in contact with the saturated media. The excavated soil (0-1 m, 1-1.6 m) (figure 7.7.1.3) had been sieved at 2 cm on site in order to remove the unwanted materials like cobbles and glasses, finer fraction of soil had been stored into glass container. Any quartering procedure had been adopted for soil homogenization. Once soil samples were collected, they get stored into cooling boxes (4 ^{o}C) and sent to the laboratory. Soil samples were extracted from hollow punches once arrived into the laboratory.

Fig. 7.7.1.2 Soil extracted from trenches from ground level to 1 m depth.

Fig. 7.7.1.3 Extracted soil sampling and samples extraction by probing .

Once get into the R&C laboratory, samples get milled by a rubber grinder and further sieved at 2mm; just finer fraction of 2 mm get analyzed. On each samples physical analysis to assess pH, structure and 105 °C residue; chemical analysis in order to assess the presence of pollutants above law limits; chemical analysis in order to assess the Total Mercury concentration; chemical analysis in order to assess the speciation of Mercury had been performed.

Chemical analysis results had shown that just Mercury concentration were above the law limits among the whole set of target contaminant; on the other hand, examples of results of the total Mercury assessment and physical properties of soil samples are reported in tables 7.7.1.1 and 7.7.1.2. It should be pointed out that total Mercury concentration were detected thanks to the application of two validated method of metal extraction (DM 13/09/1999 SO n°185 GU n° 248 21/10/1999) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (EPA 6010C 2007) during the tests.

Tab. 7.7.1.1 Example of R&C lab results on total Mercury analysis; soil sample at 0-1m depth.

Test	**U.M.**	**Value**	**Expected approximation**	**Limit value**	**Detection limit**
Structure (2mm-2cm)	g/kg	187	-		1
105 °C residue	%	89.3	±4.4		0.1
105 °C residue of air dried fine fraction	%	99.4	±3.6		0.1
Total Mercury	mgHg/kgd.m.	36.5	±5.4	5	0.1

Tab. 7.7.1.2 Example of R&C lab results on total Mercury analysis; soil sample at 1-1,6 depth.

Test	**U.M.**	**Value**	**Expected approximation**	**Limit value**	**Detection limit**
Structure (2mm-2cm)	g/kg	2.68	-		1
105 °C residue	%	81.7	±5.2		0.1
105 °C residue of air dried fine fraction	%	97.0	±3.5		0.1
Total Mercury	mgHg/kgd.m.	0.6	±0.19	5	0.1

Data obtained by the total Mercury assesment (performed on a total amount of 19 soil samples) reveals that Mercury contamination is heterogenously spread over the area both in terms of quantity and depth. In particular, minimum concentration for soil samples at 0-1 m was found to be close to the law limit 5 mg of total Mercury per kg of dry soil (7.5 mg/kg found at 3-A trecnch) while maximum concetration at similar depth was asses at 135 mg of total Mercury per kg of dry soil (9-A trench); any of the soil sample at 0-1m was found to be lower than the law limit. On the other hand, for 1-1.6 m soil samples minimum concetration was found to be 0.183 mg of total Mercury per kg of dry soil (2-B trench) while maximum value was found in 9-B trench sample at 128 mg of total Mercury per kg of dry soil; three samples were found to be lower than the law limits. Concerning Mercury speciation, analysis were conducted by following the above mentioned R&C's method on the 2 mm fraction of four soil samples. Speciation results for both 0-1m and 1-1.6m depth are reported in the following tables.

Tab. 7.7.1.3 Example of R&C lab results on Mercury speciation analysis; soil sample TR 4-A, 0-1m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	280	0.1
Water soluble Mercury	mgHg/kgd.m.	0.3	0.1
Elemental Mercury	mgHg/kgd.m.	14.3	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1	0.1
Calomel	mgHg/kgd.m.	7.2	1

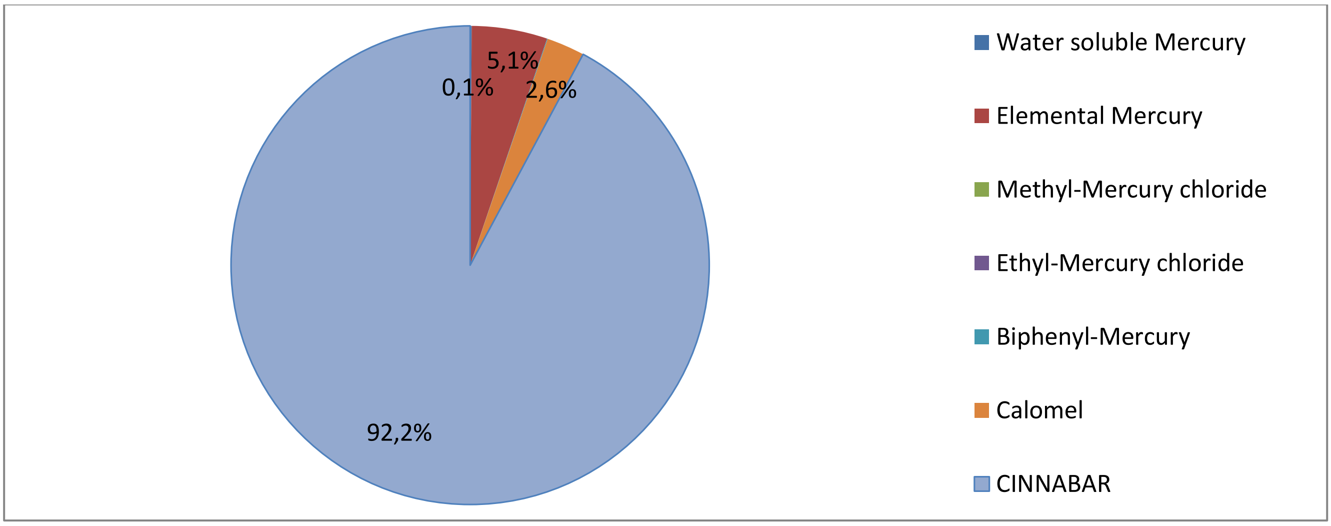


Fig. 7.7.1.4 TR 4-A Mercury fractionation.

Tab. 7.7.1.4 Example of R&C lab results on Mercury speciation analysis; soil sample TR 4-B, 1-1,6m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	36	0.1
Water soluble Mercury	mgHg/kgd.m.	<0.1	0.1
Elemental Mercury	mgHg/kgd.m.	3.3	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1	0.1
Calomel	mgHg/kgd.m.	1.0	1

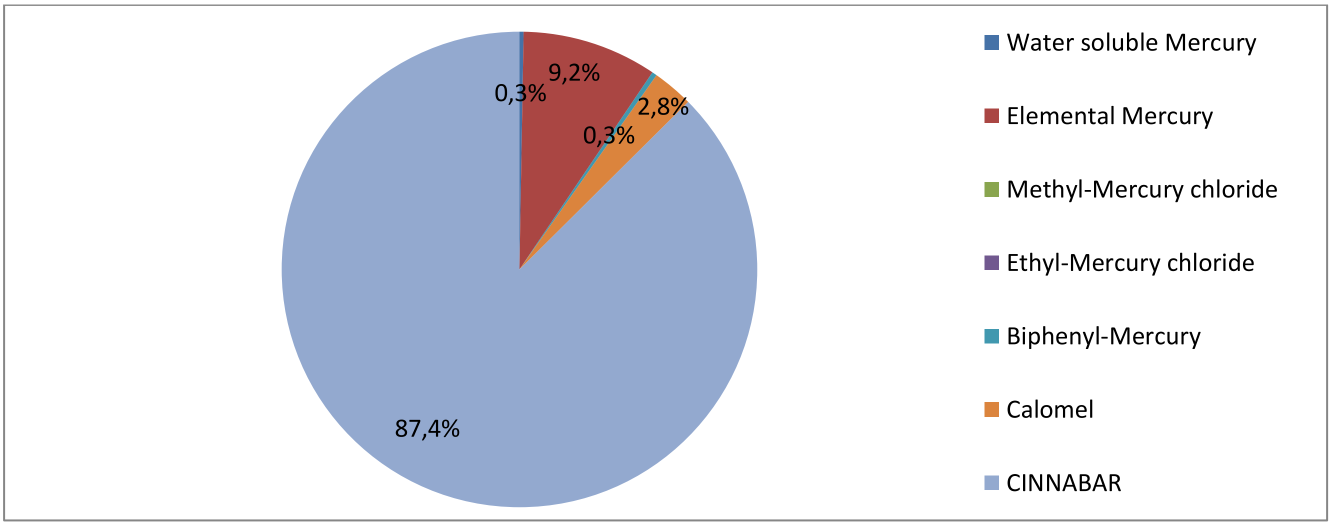


Fig. 7.7.1.5 TR 4-B Mercury fractionation.

Tab. 7.7.1.5 Example of R&C lab results on Mercury speciation analysis; soil sample TR 9-A, 0-1m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	118	0.1
Water soluble Mercury	mgHg/kgd.m.	0.5	0.1
Elemental Mercury	mgHg/kgd.m.	6.3	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1	0.1
Calomel	mgHg/kgd.m.	9.5	1

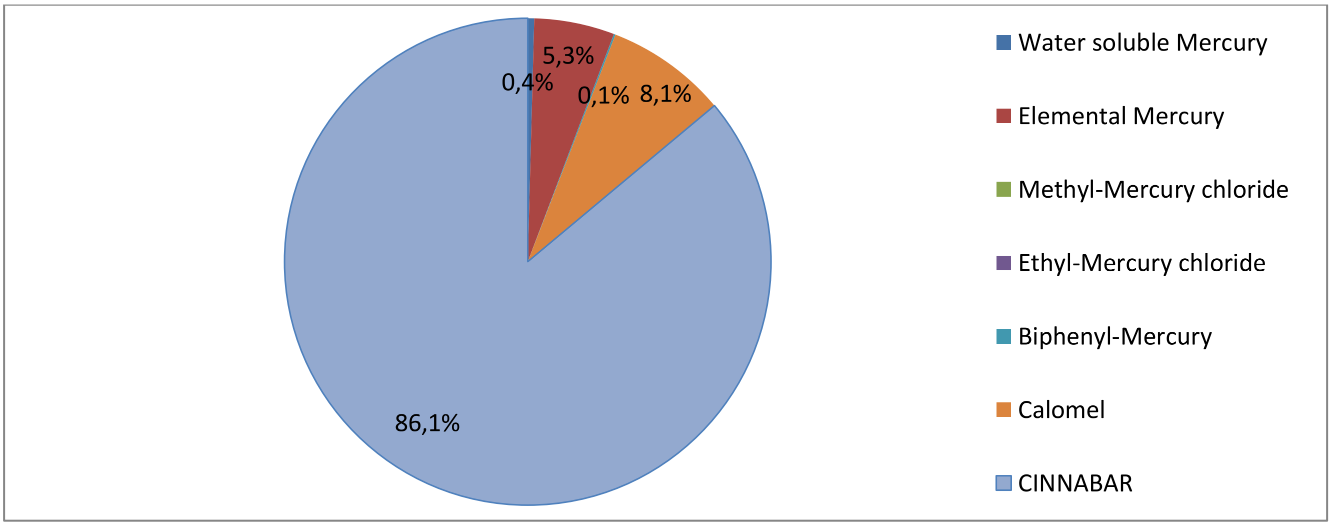


Fig. 7.7.1.6 TR 9-A Mercury fractionation.

Tab. 7.7.1.6 Example of R&C lab results on Mercury speciation analysis; soil sample TR 9-B, 1-1,6m depth.

Test	**U.M.**	**Value**	**Detection limit**
Aqua regia extractable Total Mercury	mgHg/kgd.m.	133	0.1
Water soluble Mercury	mgHg/kgd.m.	0.2	0.1
Elemental Mercury	mgHg/kgd.m.	5.2	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1	0.1
Calomel	mgHg/kgd.m.	3.3	1

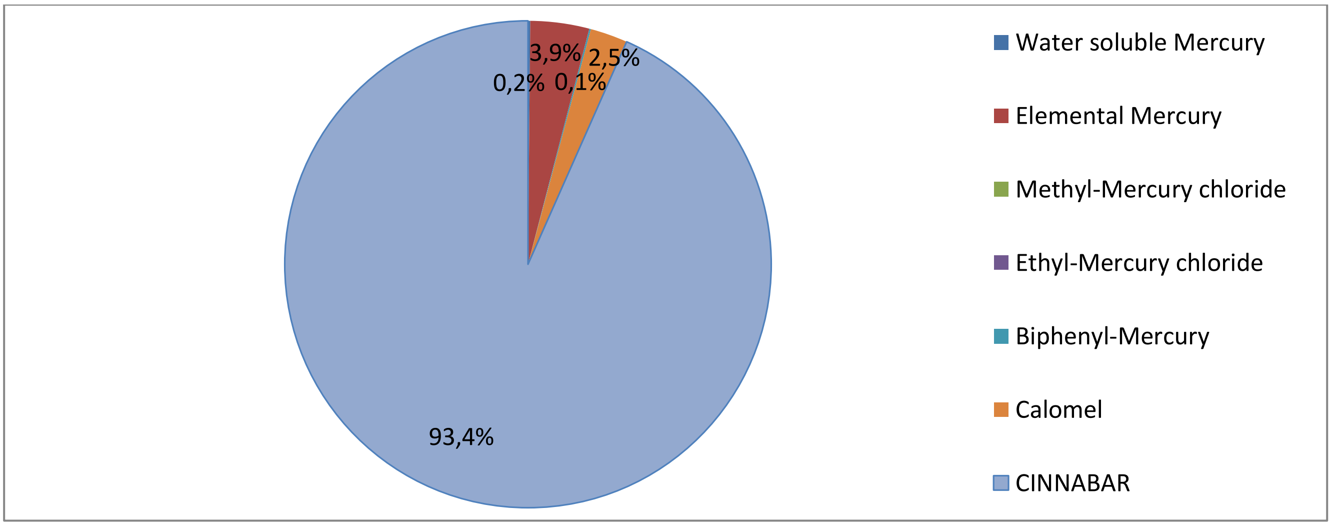


Fig. 7.7.1.7 TR 9-B Mercury fractionation.

Speciation results seems to be in line with past speciation studies reported by Boszke *et al.*, 2008; more precisely it could be noticed that: organic forms of Mercury (such as Methyl-Mercury chloride, Ethyl-Mercury chloride, Biphenyl-Mercury) are present in percentages less than 2% and into absolute concentrations similar to other Mercury contaminated sites; water soluble fraction of Mercury is present with percentages on the total Mercury in the ranges of 0.1% and absolute concentrations close to the detection limits, even in this case similar values had been experienced in literature; metallic Mercury had been found to be present into a smaller fraction in comparison with other studies, percentages on the total Mercury (5-8%) are significantly lower while absolute concentrations (3-14 mg/kg) may be compared with values found into a similar contaminated soil. Concerning residual fractions of Mercury such as HgS and Calomel, the used method seems to be affected by uncertainty into the calomel fraction evaluation; however, once the cinnabar fraction was calculated as the difference between the total mercury and other species, higher values both in percentage (close to 90%) and absolute concentrations were asses in comparison with similar soils.

7.7.2 March 2015 speciation campaign

This speciation campaign was conducted on 6 trenches located in different positions in respect of the July soil sampling; considering the fact that the site is composed by heterogeneous backfill soil, the collection of new specimens was required in order to have a more complete characterization of the soil and to confirm past speciation‘s results. In this case the location of sampling points was decided without the use of the past square-network; on the contrary, the area was considered to be divided into four parts (VP_38 piezometer was considered as the middle point) and two couples of trenches were distributed on each section. Thus, the position of each trench was fixed in correspondence of the middle point over past couples of trenches (figure 7.7.1.1). Due to the fact that any GPS localization was used during the positioning plan of sampling points, absolute benchmarks were individuated on site by using the limitation of the area as the eastern boundary of VP_38 site and the concrete foundation of the electricity network as the southern boundary. During the sampling procedure, distances between benchmarks and mutual distances between each trench were measured as reported in table 7.7.2.1.

Tab. 7.7.2.1 Absolute and mutual distances of trenches.

Trench	Southern benchmark (m)	Eastern benchmark (m)	Mutual distance (m)
TR11	5.7	11.5	-
TR12	5.7	24.5	13
TR13	6	35.5	11
TR14	6	45.5	10

Fig. 7.7.2.1 Planar view of the area and new sampling trenches (red dots).

Taking into consideration the old configuration of trenches, a representation of new sampling point‘s positions is presented in figure 7.7.2.1. Trenches number 15 and 16 were not excavated in the VP_38 site but into a closer mercury contaminated area that was planned to be treated by the same ECRT remediation. It should be underlined that security measures were adopted during the entire sampling and in particular each operator was equipped by a gas mask (to avoid inhalation of volatile fractions of Mercury), a coverall (to avoid dermal contact with contaminated soil) and an helmet. In parallel, every time the extracted soil was temporary stored on the ground, the presence of VOC and volatile Mercury fraction were asses by the use of gas indicator.
As it had been previously discussed, specimen‘s collection was focused just on the unsaturated portion of soil consequently, before soil sampling, groundwater table level was measured by the use of a level indicator inside the VP_38 piezometer. Once water table was assess to be at -1.5 m depth, soil collection was planned to be divided into A samples (0-1 m depth) and B samples (1-1.5 m depth). Trenches had been dig by the use of an excavator while the depth of each sampling point had been checked manually by the use of a measuring tape; in this way, it was possible to check when the operator had to put aside B soil rather than A soil just a function of depth. Example of the procedure of digging and depth measuring is reported in figures 7.7.2.3.

Fig. 7.7.2.3 Trench digging and depth measuring procedure.

As it could be seen from figures 7.7.2.4, the extracted soil (A) is composed by heterogeneous fractions of cobbles, wastes and backfill soil of different nature; this layer of artificial soil had been found to be present from 0 to almost 60-100 cm in depth. More precisely, backfill soil stratigraphy had revealed the presence of backfill soil of vegetal nature (0-30 cm depth; brown color) and backfill soil of gravel nature (30-60 cm depth; black color). It should be pointed out that during the soil sampling of the A fraction were often found materials of a great size and abundance that were thought to be bitumen and gypsum working wastes.

Fig. 7.7.2.4 Examples of A extracted soil and its stratigraphy.

On the other hand B fraction of soil had been found to be composed by more finer and cohesive particles that varies from sandy-silt to clay (figure 7.7.2.5); more precisely, bright gray sandy-silt with ocher stripes was found at an averaged depth of 60 to 120 cm from the ground level, while sandy-clay and clay were found from 120 to 150 cm in depth. Just in one case water table had reached the bottom of the trench that was composed mainly by sandy material.

Fig. 7.7.2.5 Examples of B extracted soil and its stratigraphy.

Similarly to the past speciation campaign, soil samples were composed by collecting different aliquots from the A or B pile; thus, an higher homogenization of the soil could be achieved in comparison with the vertical collection of samples from the side of the trench. Any quartering procedure had been used during the sample collection due to the small entity of the sample itself;

anyhow, each aliquot were sieved at 2 cm in order to remove coarser fraction of soil and the finer part (1 kg standardized sample) was temporary stored into an HDPE bag and then sealed into a glass bin (figure 7.7.2.6). HDPE and glass bins were chosen to prevent any chemical changing of the soil composition during the sampling operations; in parallel, during the transport to the laboratory, samples were refrigerated at 4 ^{o}C. Same sampling procedure was performed into trenches 15 and 16, similar characteristics of the soil were evident.

Fig. 7.7.2.6 Soil sieving at 2cm and sample storage in glass bins.

During the total Mercury analysis it was found that, among the 8 samples that were investigated in March 2015, 4 specimens had concentrations lower than the target value imposed by the Ministry. So, speciation analysis were performed just on the soil samples that were found to have total Mercury concentrations higher than 13 mg/kg. Even in this speciation campaign, it was proved that Mercury contamination is heterogenously spread over the area both in terms of quantity and depth. In fact, although 3 samples were found to have concentration close to the target values, an hot spot of 431 mg/kg was found on 0-1m depth in 14-A trecnch. As it had been done for the results obtained on July 2014, in the following tables will be reported the Mercury fractionation. It should be reminded that the total Mercury values reported in these tables had been calculated by the R&C lab method. Unfortunately, during the speciation analysis the thermodesorber device was found to be affected by failure of some mechanical components so, any information about the organic fractions and calomel was available soon enough for the thesis conclusion. However, the fact that those values were not assessed does not represent an issue for the thesis purposes; past speciation results had shown that those concentrations were below or close to the detection limits and thus may be considered negligible in terms of percentages on total Mercury. Furthermore, as it had previously mentioned, the feasibility study is based on the quantification of the target species of Mercury (metallic Mercury) that may be removed by the

ECRT; metallic Mercury concentration were successfully calculated by the use of a static ahead space Gas Chromatography-Mass spectrography device. Missing data were assumed to be close to the results obtained in July 2014.

Tab. 7.7.2.2 Example of R&C lab results on Mercury speciation analysis; soil sample TR 11-A, 0-1m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	152	0.1
Water soluble Mercury	mgHg/kgd.m.	0.2	0.1
Elemental Mercury	mgHg/kgd.m.	4.1	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1*	0.1
Calomel	mgHg/kgd.m.	10*	1

Tab. 7.7.2.3 Example of R&C lab results on Mercury speciation analysis; soil sample TR 11-B, 1-1.6m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	103	0.1
Water soluble Mercury	mgHg/kgd.m.	<0.1	0.1
Elemental Mercury	mgHg/kgd.m.	3.7	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1*	0.1
Calomel	mgHg/kgd.m.	3*	1

Tab. 7.7.2.5 Example of R&C lab results on Mercury speciation analysis; soil sample TR 12-B, 1-1.6m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	23.8	0.1
Water soluble Mercury	mgHg/kgd.m.	<0.1	0.1
Elemental Mercury	mgHg/kgd.m.	<1	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	<0.1*	0.1
Calomel	mgHg/kgd.m.	1*	1

Tab. 7.7.2.6 Example of R&C lab results on Mercury speciation analysis; soil sample TR 13-A, 0-1m depth.

Test	**U.M.**	**Value**	**Detection limit**
Aqua regia extractable Total Mercury	mgHg/kgd.m.	53	0.1
Water soluble Mercury	mgHg/kgd.m.	<0.1	0.1
Elemental Mercury	mgHg/kgd.m.	<1	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	<1*	0.1
Calomel	mgHg/kgd.m.	1*	1

Tab. 7.7.2.7 Example of R&C lab results on Mercury speciation analysis; soil sample TR 13-B, 1-1.6m depth.

Test	**U.M.**	**Value**	**Detection limit**
Aqua regia extractable Total Mercury	mgHg/kgd.m.	15.9	0.1
Water soluble Mercury	mgHg/kgd.m.	<0.1	0.1
Elemental Mercury	mgHg/kgd.m.	<1	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	<1*	0.1
Calomel	mgHg/kgd.m.	<1*	1

Tab. 7.7.2.7 Example of R&C lab results on Mercury speciation analysis; soil sample TR 14-A, 0-1 m depth.

Test	**U.M.**	**Value**	**Detection limit**
Aqua regia extractable Total Mercury	mgHg/kgd.m.	431	0.1
Water soluble Mercury	mgHg/kgd.m.	0.9	0.1
Elemental Mercury	mgHg/kgd.m.	17.6	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1*	0.1
Calomel	mgHg/kgd.m.	15*	1

Tab. 7.7.2.7 Example of R&C lab results on Mercury speciation analysis; soil sample TR 14-B, 1-1.6 m depth.

Test	U.M.	Value	Detection limit
Aqua regia extractable Total Mercury	mgHg/kgd.m.	112	0.1
Water soluble Mercury	mgHg/kgd.m.	0.1	0.1
Elemental Mercury	mgHg/kgd.m.	3.4	1
Methyl-Mercury chloride	mgHg/kgd.m.	<0.5*	0.5
Ethyl-Mercury chloride	mgHg/kgd.m.	<3*	3
Biphenyl-Mercury	mgHg/kgd.m.	0.1*	0.1
Calomel	mgHg/kgd.m.	3*	1

Similarly to the results proposed in the previous paragraph, concentrations of water soluble Mercury were not asses in the majority of the soil samples with the exception of TR 11-A, TR 14-B and TR 14-A that shows the highest concentration ever (0.95 mg/kg).

Tab. 7.7.2.8 Comparison between speciation results of July 2014 and March 2015.

Sample	Total Mercury (mgHg/kgd.m.)	Metallic Mercury (mgHg/kgd.m.)
TR 4-A	280	14.3
TR 4-B	36	3.3
TR 9-A	118	6.3
TR 9-B	133	5.2
TR 11-A	152	4.1
TR 11-B	103	3.7
TR 12-B	23.8	<1
TR 13-A	53	<1
TR 13-B	15.9	<1
TR 14-A	431	17.6
TR 14-B	112	3.4

As it could be seen in table 7.7.2.8, results of March 2015 speciation show, with the exception of few samples, a lower concentration of total Mercury in comparison with July 2014 results; most importantly, metallic Mercury concentrations lower than the detection limit were found in the samples related to lower concentration of total Mercury. At the same time it should be pointed out that, with the exception of TR 14-A, the whole set of results of 2015 shows Metallic Mercury percentages in the ranges of 1.5%-2% of total Mercury that are almost half of the percentages found during the past speciation. Even if a direct proportionality between concentrations of total Mercury and Metallic Mercury seems to be plausible, the comparison with the lower total Mercury concentration of July 2014 (TR 4-B) and similar concentrations of March 2015 (TR 12-B, TR 13-A) evidently fail this hypothesis. More evidently, the heterogeneity of the results shows the great variability of the Mercury pollution related to the nature of the backfill soil. On the other hand, it seems to be reasonable to expect that Cinnabar represent the major part of the total Mercury concentration.

7.8 Risk assessment and target concentration calculation

As it had been previously mentioned, the aim of the risk analysis that had been performed was to evaluate, without the presumption of being comparable with a detailed risk assessment, the comparison of the two different scenarios that had been discussed in this study. It should be pointed out that recently the Italian Health Institute had introduced the characteristics of the Mercury‘s species on its database thus confirming the importance of the metal speciation during risk assessment.

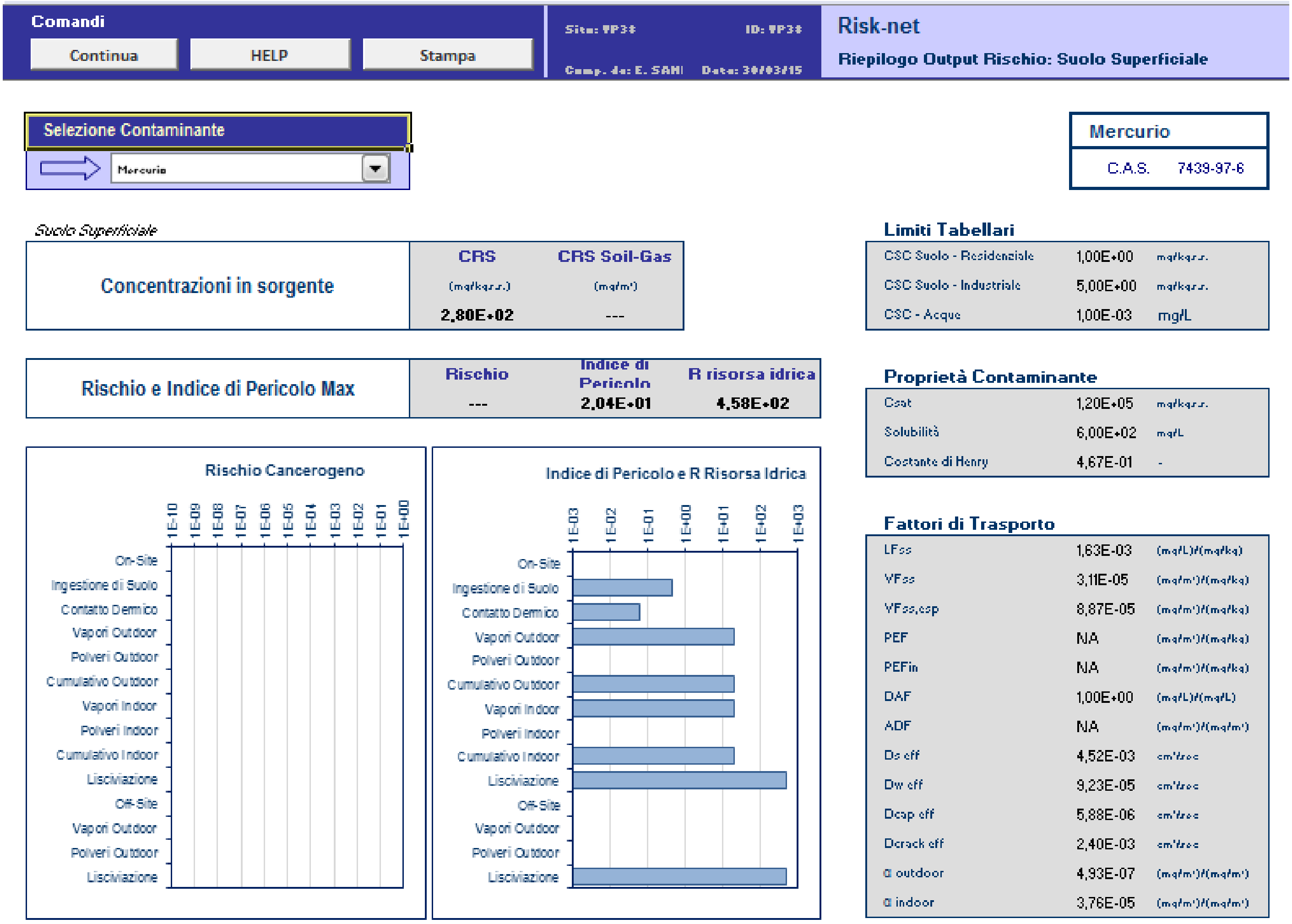
Evaluation of the risk was calculated for both superficial and deep soil (unsaturated fractions) taking into considerations the transport pathways of inhalation, ingestion and run off to the groundwater. The algorithms were applied in the forward modality to calculate risk while backward modality was applied to calculate the cleanup levels (CSR). For human health, the risk is considered acceptable if the cumulative Hazard Index (HI) is lower than 1 (non-carcinogenic compounds); in parallel, for the risk acceptability of the groundwater bodies the Risk for GroundWater (RGW) index (calculated as the ratio between calculated concentration on the groundwater and limit concentrations defined by law) must be lower than 1.

7.8.1 Tot_Hg approach

About the total Mercury data, as it could be seen in figure 7.8.1.1, the Risknet software had calculated an HI of 20 in relation to both indoor and outdoor environments for superficial soil; more precisely, concerning the outdoor ambient, inhalation of vapors was the main pathway of risk with an HI of 19.8 while ingestion and dermal contact are in the range of 10^{-1} and 10^{-2}. Hazardous Index of 20.4 was calculated for inhalation at indoor ambient. On the other hand, concerning the protection of ground water, the leaching from soil of Mercury seems to greatly affects its preservation; a value of 458 was estimated for RGW. Considering the deep soil, an HI of 6.4 and 9.4 were calculated for outdoor and indoor ambient respectively; as it could be easily guessed, pathways of inhalation are sensibly reduced with the increasing of depth. Concerning the risk for groundwater related to deep soil, RGW value of 348 had been estimated; in comparison with the superficial soil, the leaching to groundwater has a more important contribute but source concentration were significantly lower in deep soil. Concerning the calculation of target concentration, the CSR had been assessed to be 0.612 mg/kg for superficial soil and 0.382 mg/kg for deep soil; some considerations should be further analyzed.

The CSR seems to be greatly affected by the leaching pathway; the cleanup levels (CSR) related to groundwater protection are the most precautionary among the whole set of results; in fact, cleanup target concentration for the cumulative contributes of ingestion, inhalation and dermal contact were close to 14 mg/kg for both indoor and outdoor ambient. The risk related to leaching from polluted soil to groundwater is probably overestimated as the fate and transport model for this pathway is quite simple and conservative. As a matter of fact, during the past characterization of the area, groundwater was not found to be affected by mercury pollution.

Fig. 7.8.1.1 Superficial soil‘s risk assessment output.



Site: TP38 ID: TP38
Comp. da: E. SANI Data: 30/03/15

Riepilogo Output Rischio: Suolo Superficiale

Mercurio

Mercurio
C.A.S. 7439-97-6

Suolo Superficiale

	CRS (mg/kg s.s.)	CRS Soil-Gas (mg/m^3)
Concentrazioni in sorgente	2,80E+02	---

	Rischio	Indice di Pericolo	R risorsa idrica
Rischio e Indice di Pericolo Max	---	2,04E+01	4,58E+02

Limiti Tabellari

CSC Suolo - Residenziale	1,00E+00	mg/kg s.s.
CSC Suolo - Industriale	5,00E+00	mg/kg s.s.
CSC - Acque	1,00E-03	mg/L

Proprietà Contaminante

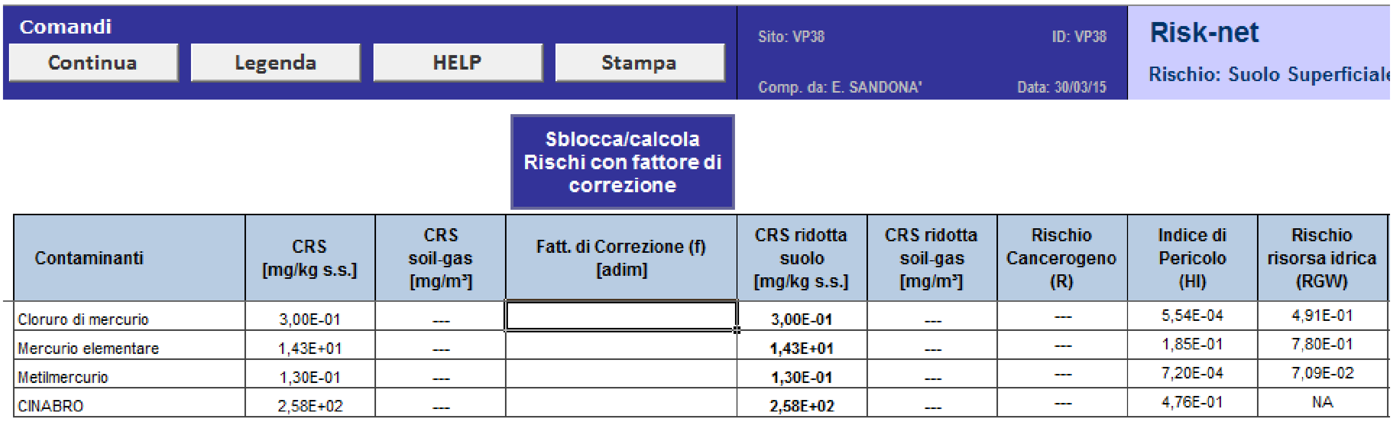
Csat	1,20E+05	mg/kg s.s.
Solubilità	6,00E+02	mg/L
Costante di Henry	4,67E-01	-

Fattori di Trasporto

LFss	1,63E-03	(mg/L)/(mg/kg)
VFss	3,11E-05	(mg/m^3)/(mg/kg)
VFss,esp	8,87E-05	(mg/m^3)/(mg/kg)
PEF	NA	(mg/m^3)/(mg/kg)
PEFin	NA	(mg/m^3)/(mg/kg)
DAF	1,00E+00	(mg/L)/(mg/L)
ADF	NA	(mg/m^3)/(mg/m^3)
Ds eff	4,52E-03	cm^2/sec
Dw eff	9,23E-05	cm^2/sec
Dcap eff	5,88E-06	cm^2/sec
Dcrack eff	2,40E-03	cm^2/sec
α outdoor	4,93E-07	(mg/m^3)/(mg/m^3)
α indoor	3,76E-05	(mg/m^3)/(mg/m^3)

7.8.2 Speciation_Hg approach

Concerning the results of the risk analysis with the speciation data, it should be reminded that they were obtained by the use of a recently released software (Risknet 2.0, April 2015) that was equipped with a more complete database in comparison with the old version of the software. In fact, the database of the software was updated with the most recent version of ISS-ISPESL database. More precisely, in the 2015 database the competent authorities had introduced three species of Mercury of most concern in regard of risk assessment; Mercuric Chloride was thought to represent the water soluble fraction and thus the risk related to leaching and water pollution, Methyl-Mercury was related to the ingestion and bioaccumulation assessment while Metallic Mercuric was considered to represent the inhalable fraction. This upgrade is a step forward in comparison to the old database, but still a lack of information seems to affect the characterization of the compounds; more in details, the fact any information about solubility and k_d had been defined for Methyl-Mercury seems to force the software to work with one-pathway-limited compounds rather than consider the compound to be susceptible to ingestion, dermal contact, inhalation or leaching. However, the brief literature review that had been conducted allowed the use of a more complete and realistic database. Concerning the superficial soil, as it could be seen in figure 7.8.2.1, none of the input species had been found to generate risk for health or for ground water; in particular: cumulative risk of ingestion, inhalation and dermal contact was close to 10^{-4} for both Mercuric Chloride and Methyl-Mercury and close to 10^{-1} for Metallic Mercury and Cinnabar. Inhalation of Metallic Mercury was related to an HI of 10^{-2} for both indoor and outdoor ambient; it should be reminded that indoor risk assessment was performed using an highly precautionary inputs about building's parameters. Hazard Index for Cinnabar ingestion were calculated in ranges of 10^{-1} while Hazard Index for Mercuric Chloride and Methyl-Mercury ingestion were assessed at 10^{-4}. These results should be analyzed in light of the input fractionation which revealed that almost 90% was present as Cinnabar species.



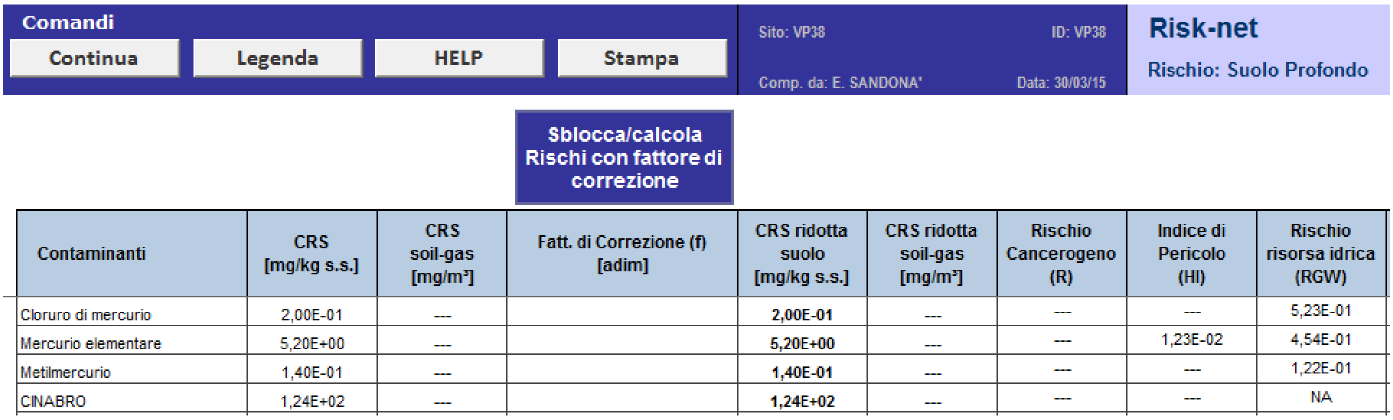
Sito: VP38
ID: VP38
Comp. da: E. SANDONA'
Data: 30/03/15

Risk-net
Rischio: Suolo Superficial

Contaminanti	CRS [mg/kg s.s.]	CRS soil-gas [mg/m³]	Fatt. di Correzione (f) [adim]	CRS ridotta suolo [mg/kg s.s.]	CRS ridotta soil-gas [mg/m³]	Rischio Cancerogeno (R)	Indice di Pericolo (HI)	Rischio risorsa idrica (RGW)
Cloruro di mercurio	3,00E-01	---		3,00E-01	---	---	5,54E-04	4,91E-01
Mercurio elementare	1,43E+01	---		1,43E+01	---	---	1,85E-01	7,80E-01
Metilmercurio	1,30E-01	---		1,30E-01	---	---	7,20E-04	7,09E-02
CINABRO	2,58E+02	---		2,58E+02	---	---	4,76E-01	NA

Fig. 7.8.2.1 Superficial soil's risk assessment output.

Similarly, deep soil risk assessment had revealed, for Metallic Mercury inhalation, HI of 10^{-3} and 10^{-2} respectively for outdoor and indoor ambient. RGW values of 10^{-1} were calculated for Mercuric Chloride, Methyl-Mercury and Metallic Mercury. Summary of output data is given in figure 7.8.2.2.



Sito: VP38
ID: VP38
Comp. da: E. SANDONA'
Data: 30/03/15
Rischio: Suolo Profondo

Contaminanti	CRS [mg/kg s.s.]	CRS soil-gas [mg/m³]	Fatt. di Correzione (f) [adim]	CRS ridotta suolo [mg/kg s.s.]	CRS ridotta soil-gas [mg/m³]	Rischio Cancerogeno (R)	Indice di Pericolo (HI)	Rischio risorsa idrica (RGW)
Cloruro di mercurio	2,00E-01	---		**2,00E-01**	---	---	---	5,23E-01
Mercurio elementare	5,20E+00	---		**5,20E+00**	---	---	1,23E-02	4,54E-01
Metilmercurio	1,40E-01	---		**1,40E-01**	---	---	---	1,22E-01
CINABRO	1,24E+02	---		**1,24E+02**	---	---	---	NA

Fig. 7.8.2.2 Deep soil's risk assessment output.

In line with the Hazard Index results, superficial soil target concentrations of Cinnabar and Metallic Mercury were found to be higher than the previously calculated total Mercury target concentration. More precisely, cumulative target concentration for ingestion, inhalation and dermal contact of 540 mg/kg and 70 mg/kg were found for Cinnabar and Metallic Mercury respectively. In parallel, target concentration of 18 mg/kg were calculated for groundwater protection. Concerning Mercuric Chloride and Methyl-Mercury, target concentrations for groundwater protection of 10^{-1} mg/kg and 2 mg/kg were respectively calculated; target concentrations for human health were in the order of magnitude of 10^{2}. Target concentrations for deep soil were found to be higher than the saturation concentration of each species.

8. CONCLUSIONS

The industrial site of Porto Marghera had been demonstrated to be one the most polluted area of the Italian region; the characterization of top soil, soil and groundwater had revealed a severe contamination by chlorine compounds and metals in all the environmental media. The great extent of the site and the heterogeneous kind of pollutants that were found during the sampling, heavily affected the development of the remediation campaign; in parallel, high capital costs for the recovery make Porto Marghera to be less desirable in comparison with other industrial districts. Even if huge actions on pollution containment had been already concluded among the area, the remediation of both soils and ground water is still in its early stages. Explanation of this delay may be related to several different reasons that vary from site to site; at the same time, during the development of this thesis, the great limitation given by a fuzzy and not always effective legislation on the remediation of contaminated sites was evident. More precisely, in this study the importance of the use of a preliminary tool such as metal speciation was evaluated and underlined in order to assess more realistic scientific-based aims for risk assessment and site‘s remediation.

The review of previously approved projects and the risk analysis had proved the lack of a scientific approach during the evaluation of remediation‘s aims for the mercury contaminated site in exam; in parallel, thanks to a literature review on Mercury speciation, it seemed evident that law limit expressed as total Mercury concentration was a sort of incomplete data. Furthermore, past field test conducted on mercury contaminated areas among the industrial site had demonstrated the ability of the chosen ECRT technique to reduce, in combination with a Iodine solution, the total Mercury concentration in soil; more recently, thanks to the research study conducted by the University of Ferrara, mercury speciation analysis were found to be fundamental for the scaling up of the application and its cost analysis. So, in light of considerations mentioned above, the metal speciation has a double role during sites remediation: on one hand it should be used by the authorities as a scientific data for risk assessment approval and remediation aim‘s evaluation, on the other hand the private company should take advantage of speciation analysis in order to assess in advance whether the chosen technique is able to reach target concentrations with sustainable costs. As it is widely accepted, higher risks are associated to mobile fractions of metals (such as Hg^0, Methyl-Mercury) while on the contrary, less mobile or immobile forms of the same element (such as HgS) may be considered unable to reach targets of risk. The assessment of the mobile and immobile fractions is evidently of primary importance in order to fix the acceptable residue concentration for healthy safeguard and for remediation‘s target. In parallel, concerning the latter role, it could be stated that the use of speciation analysis as a preliminary tool for ECRT feasibility assessment is a step forward in comparison to common practices based on literature study cases total Mercury removal. In fact, the possibility to known in advance the quantity of Mercury that could be mobilized and consequently removed (as a function of its mobility and species) allows the proper dosage of chemical solutions to be used and thus reduce the capital costs of the application.

Concerning Mercury speciation, it should be pointed out that any of the commonly used methods for ‗classic‘‘ metal speciation could be used due to the fact that Mercury had markedly different chemical proprieties in comparison with Fe, Mn, Cu, Ni; as a consequence, even if standardized techniques had been proposed and validated, the lack of a unique practice led to possible misunderstanding during the evaluation of speciation results. During this study, standardized methods for total Mercury assessment and innovative Mercury speciation technique were employed; the results of the analysis had demonstrated the reliability of the former and the working in progress of the latter. However, even if a wider set of data is advisable, by the evaluation of speciation results two fundamental evidences should be stressed out: the sum between organic and metallic forms of Mercury (considered to be the mobile fractions) reaches averagely 2%-10% of the total Mercury present in the soil sample; simultaneously, the stable form of Mercury (considered as Calomel) is present in all samples with percentages that vary from 30% to 200% of the metallic form while Cinnabar fraction represent up to the 90% of the total Mercury. As a consequence, by considering the effectiveness and the mechanism of the application, it seems reasonable to assume that just 2%-10% of the total Mercury concentration could be the target of the remediation; in parallel, due to the physical limitations of the technique and to site specific impediment it could be expected that a little mobilization and removal of stable forms of Mercury could be achieved. By analytical calculations, final concentrations of about 70%-80% of the initial total Mercury concentrations may be expected; thus, even if higher removal efficiencies may be reached once the application is running, the target value of 13 mg totHg/kg d.m. seems not to be achievable by the use of the current ECRT application. At the same time, by the use of a recently released software, it was possible to prove that any risk is associated to the different species of Mercury found on site and thus the clean-up target of total Mercury seems to be an inadequate overestimation of the real situation.

It seems to be evident that the speciation analysis had revealed the incompatibility between the limitations of the technique (in terms of both efficiency and cost-benefits) and the roughness of the past risk evaluation; as a consequence, during this study different solutions to the proposed problem had been sized up. Two main alternatives were considered: landfilling of the contaminated soil may guarantee the complete removal of the source of pollution and the secure fulfillment of the law limit requirement; at the same time, as it is widely accepted, landfilling is not a suitable solution in terms of sustainability and costs (with an average cost of 170 €/t, almost 500,000 € were calculated as overall expense of excavation, analysis, transport and landfilling). On the other hand, thanks to the scientific support of speciation analysis and further improvements of the ECRT technique obtained by the University of Ferrara, the hypothesis that seems to be more advisable is to present to the competent authorities a modified remediation plan that includes more specific and detailed aims.

It should be pointed out that further research should be performed about the scale up of the technique proposed by Rosestolato *et al.,* 2015 and about a more detailed risk analysis on Mercury‘s species; at the same time, further speciation tests seems to be required in order to give more reliability on the method used during this study.

References

Acar Y.B., Gale R.J., Alshawabkeh A.N., Marks R.E., Puppala S., Bricka M., Parker R. (1995). Electrokinetic remediation: basics and technology status. Journal of Hazardous Materials 40, 117-137

Accordo di programma per la chimica di Porto Marghera (1999). Regione Veneto

Ahalya N., Ramachandra T.V., Kanamadi RD. (2003). Biosorption of Heavy Metals. Research Journal Of Chemistry And Environment 7, 101-109

Ali H., Khan E., Muhammad A.S. (2013). Phytoremediation of heavy metals—Concepts and applications. Chemosphere 91, 869–881

Allison J.D. and Allison T.L. (2005). Partition coefficients for metals in surface water, soil, and waste.
U.S. Environmental Protection AgencyOffice of Research and Development Washington, DC. EPA/600/R-05/074

Alshawabkeh A.N., Bricka R.M., Gent D.B. (2005). Pilot-scale electrokinetic cleanup of lead-contaminated soils. Journal of Geotechencial and Geoenvironmental Engineering 131, 283-291

Babko S.V., Montgomery J.L., Battleson D.M., Whitworth C.G., Sears J., Sunner J., Gingery D. (2001). Mercury speciation analysis by gas chromatography/electron impact/mass spectrometry. WM'01 Conference, February 25-March 1, 2001, Tucson, AZ

Barizza S. (2008/2009). La laguna tra residualità e ambiente. Porto Marghera: nascita, sviluppo e attualità. Assessorato Ambiente - Osservatorio Naturalistico della Laguna - Centro Studi Riviera del Brenta. La laguna di Venezia: genesi, evoluzione, naturalità e salvaguardia

Bloom N.S., Preus E., Katon J., Hiltner M. (2003). Selective extractions to assess the biogeochemically relevant fractionation of inorganic Mercury in sediments and soils Analytica Chimica Acta 479, 233–248

Bolan N., Naidu R, Syer J.K., Tillman R. (1999). Surface charge and solute interactionism in soils. Advances in Agronomy 67, 88–141

Bolan N., Kunhikrishnan A., Thangarajana R., Kumpiene J., Park J., Makino T., Kirkham M.B., Scheckel K. (2014). Remediation of heavy metal(loid)s contaminated soils – To mobilize or to immobilize? Journal of Hazardous Materials 266, 141– 166

Bosecker K. (1997). Bioleaching: metal solubilization by microorganism. FEMS Microbiology Review 20, 591-604

Bosecker K.. (2001). Microbial leaching in environmental clean-up programmes. Hydrometallurgy 59, 245–248

Boszke L., Kowalski A., Astel A., Baranski A., Gworek B., Siepak J. (2008). Mercury mobility and bioavailability in soil from contaminated area. Environ Geol 55, 1075–1087

Chinello C., Storia di uno sviluppo capitalistico: Porto Marghera e Venezia 1951-1973, Roma, 1975, p.12

Cox C.D., Shosesmi M.A. (1996). Electrokinetic remediation of Mercury-contaminated soils using iodine/iodide lixiviant. Environmental Science Technology 30, 1933-1938

D'Aprile L. (2007). Stato di attuazione delle attivita' di bonifica e utilizzo di tecnologie innovative nei siti di interesse nazionale: casi studio. Servizio Interdipartimentale per le Emergenze Ambientali, Settore Siti Contaminati, APAT

Davis A., Bloom N.S., Que Hee. (1997). The Environmental Geochemistry and Bioaccessibility of Mercury in Soils and Sediments: A Review. Risk Analysis 17 5.

DeFlaun M.F., Condee C.W. (1997). Electrokinetic transport of bacteria. Journal of Hazardous Materials 55, 263-277

D'Emilio D., Sala V.S., Salamone R., De Battisti A., Ferro S., Ferri V., Lageman R.(2008). In-situ electrokinetic reclamation of Mercury in Porto Marghera site. Conference on: Groundwater and soil reclamation technologies. RemTech, Ferrara

Doering F., Doering N., Iovenitti J.L., Hill D.G., McIlvride W.A. (2001), Electrochemical remediation technologies for soil, sediment and ground water. Proceedings of the 2001 International Containment & Remediation Technology Conference and Exhibition, 10-13 June 2001, Orland, FL, USA.

EPA. (2007). Electrochemical Remediation Technologies (ECRTs) - In situ Remediation of Contaminated Marine Sediments; Innovative Technology Evaluation Report. EPA/540/R-04/507

Ferrarese E., Andreottola G., (2008). Electrochemical Oxidation of Soils Contaminated with Organic Pollutants, Based on the Doctoral thesis in Environmental Engineering (XX cycle) defended in February 2008 at the Faculty of Engineering of the University of Trento.

Ferrarese E., Andreottola G., Oprea I.A. (2008), Remediation of PAH-contaminated sediments by chemical oxidation, Journal of Hazardous Materials 152, 128-139.

Fitzgerald W.F., Lamborg C.H.. (2007). Geochemistry of Mercury in the Environment. Treatise on Geochemistry, Volume 9: Environmental Geochemistry, 1–47

Gadd G.M. (2009). Heavy Metal Pollutants: Environmental and Biotechnological Aspects.University of Dundee, Dundee, Scotland, UK

Gao Y., Shi Z., Long Z., Wu P., Zheng C., Hou X. (2012). Determination and speciation of mercury in environmental and biological samples by analytical atomic spectrometry. Microchemical Journal 103, 1–14

García-Rubio A., Rodríguez-Maroto J.M., Gómez-Lahoz C., García-Herruzo F., Vereda-Alonso C. (2011). Electrokinetic remediation: The use of mercury speciation for feasibility studies applied to a contaminated soil from Almadén. Electrochimica Acta 56, 9303– 9310

Garbisu C., Alkorta I. (2001). Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment. Bioresource Technology 77, 229-236

Garbisu C., Alkorta I. (2003). Basic concepts on heavy metal soil bioremediation. The European Journal of Mineral Processing and Environmental Protection 3, 58-66

Gent D.B., R. Mark Bricka R.M., Alshawabkeh A.N., Larson S.L., Fabian G., Granade S. (2004). Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics. Journal of Hazardous Materials 110, 53–62

Gomes H.I., Dias-Ferreira C., Ribeiro A.B. (2012), Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies. Chemosphere 87, 1077–1090.

Han Y., Kingston H.M., Boylan H.M., Rahman G.M., Shah S.,. Richter R.C,. Link D.D., Bhandari S. (2003). Speciation of Mercury in soil and sediment by selective solvent and acid extraction. Anal Bioanal Chem 375, 428–436

Ho Sa.V., Athmer C.J., Sheridan P.W., Shapiro A.P. (1997). Scale-up aspects of the Lasagna process for in situ soil decontamination. Journal of Hazardous Materials 55, 39-60

Hong C.O., Lee D.K., Chung D.Y., Kim P.J. (2007). Liming Effects on Cadmium Stabilization in Upland Soil Affected by Gold Mining Activity. Archives of Environmental Contamination and Toxicology 52, 496–502

Issaro N., Abi-Ghanem C., Bermond A. (2009). Fractionation studies of Mercury in soils and sediments: a review of the chemical reagents used for Mercury extraction. Analytica Chimica Acta 631 1–12

Jadia C.D., Fulekar M.H. (2009). Phytoremediation of heavy metals: Recent techniques. African Journal of Biotechnology 8, 921-928

Khan F.I., Husain T., Hejazi R. (2004). An overview and analysis of site remediation technologies. Journal of Environmental Management 71, 95–122

Kim C., Bloom N.S., Rytuba J.J., Brown G.Jr. (2003). Mercury speciation by x-ray absorption fine structure spectroscopy and sequential chemical extractions: a comparison of speciation methods. Environmental Science and Technology 37, 5102-5108

Kim S.O., Moon S., Kim K.W. (2000). Removal of heavymetals from soils using enhanced electrokinetic soil processing. Water, Air, and Soil Pollution 125, 259–272

Kim W.S., Kim S.W., Kim K.W. (2005), Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes. Journal of Hazardous Materials 118, 93–102

Kumpiene J. (2010). Trace element immobilization in soil using amendments. Trace element is soil, Wiley-Blackwel

Li Z., Yu J.W., Neretnieks I. (1996). A new approach to electrokinetic remediation of soils polluted by heavy metals. Journal of contaminant hydrology 22, 241-253

Maini G., Sharman A.K., Knowles C.J., Sunderland G., Jackman S.A. (2000). Electrokinetic remediation of metals and organics from historically contaminated soil. Journal of Chemical Technology and Biotechnology 75, 657 664

Master plan per la bonifica dei siti inquinati di porto marghera (2000). Regione veneto

Mohamed A.M.O.(1996). Remediation of heavy metal contaminated soils via integrated electrochemical processes. Waste management 16, 741-747

Morales E.M. (2002). A Review of the Electrokinetic Process for Soil Remediation (REV. 1.0)

Morita M., Yoshinaga J., Edmondst J.S. (1998). The determination of Mercury species in environmental and biological samples (technical report). Pure & applied chemistry 70, 1585-1615

Mulligan C.N., Yong R.N., Gibbs B.F., (2001). Remediation technologies for contaminated soils and groundwater: an evaluation. Engineering Geology 60, 193-207

Negrete M., Luis J.J., Barboza L.. (2013). Electrokinetic remediation of Mercury- contaminated soil, from the mine El Alacran-San Jorge river basin, Cordoba – Colombia. Revista Facultad de Ingeniería Universidad de Antioquia 68, 136-146

Niroumand H., Nazir R., Kassim K.A. (2012). The Performance of Electrochemical Remediation Technologies in Soil Mechanics. International Journal of Electrochemical Science 7, 5708 – 5715

Obiri-Nyarko F.,. Grajales-Mesa S.J, Grzegorz M. (2014). An overview of permeable reactive barriers for in situ sustainable groundwater remediation. Chemosphere 111, 243–259

Page M.M., Page C.L. (2002). Electroremediation of Contaminated Soils. Journal of environmental engineering 128, 208-219.

Palmieri H.E.L., Nalini H.A.Jr., Leonel L.V., Windmoller C.C., Santos R.C., Brito W. (2006). Quantification and speciation of Mercury in soils from the Tripuı Ecological Station, Minas Gerais, Brazil. Science of the Total Environment 368, 69– 78

Pozzan A.(2014). Marghera 900. Archivi della politica e dell‘impresa del ‗900 veneziano. Fondazione Gianni Pellicani

Pulford I.D., Watson C. (2002). Phytoremediation of heavy metal-contaminated land by trees—a review. Environment International 29, 529– 540

Puppala K.S. , Alshawabkeh A.N., Acar Y.B., Gale R.J., Bricka M. (1997), Enhanced electrokinetic remediation of high sorption capacity soil. Journal of Hazardous Materials 55, 203-220

Rajendran P., Muthukrhishnan J., Gunasekaran P. (2003). Microbes in heavy metal remediation. Indian journal of experimental biology 41, 935-944

Rahner D., Ludwig G., Ro¨hrs J.(2002). Electrochemically induced reactions in soils—a new approach to the in-situ remediation of contaminated soils? Part 1: The microconductor principle. Electrochimica Acta 47, 1395–1403

Rani L., Basnet B., Kumar A. (2011). Mercury Toxicity. All India Institute of Medical Sciences, New Delhi, India

Reddy K.R., Carlos Chaparro C., Saichek R.E. (2003). Removal of Mercury from clayey soils using electrokinetics. Journal of environmental science and health A38, 307–338

Reddy K.R. and Cameselle C. (2009). Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater. Copyright © 2009 John Wiley & Sons, Inc.

Reis A.T., Coelho J.P., Rucandio I., Davidson C.M., Duarte A.C., Pereira E. (2015). Thermo-desorption: A valid tool for mercury speciation in soils and sediments? Geoderma 237-238, 98-104

Ren L., Lu H., Hea L., Zhang Y. (2014) Enhanced electrokinetic technologies with oxidization–reduction for organically-contaminated soil remediation. Chemical Engineering Journal 247, 111–124

Rosestolato D., Bagatin R., Ferro S. (2015). Electrokinetic remediation of soils polluted by heavy metals (Mercury in particular). Chemical Engineering Journal 264, 16–23

Sawada A., Morid K., Tanakaa S., Fukushima M., Tatsumic K. (2004). Removal of Cr(VI) from contaminated soil by electrokinetic remediation. Waste Management 24, 483–490

Shen Z., Zhang J., Qu L., Dong Z., Zheng S., Wang W.(2009). A modified EK method with an I-/I2 lixiviant assisted and approaching cathodes to remedy Mercury contaminated field soils. Environmental Geology 57,1399–1407

Smith K. and Huyck H.. (1999). An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals. Economic Geology 6A

Soriani S., Zanetto G. (2009). La riqualificazione delle aree portuali e industriali. l'esempio del parco scientifico e tecnologico di Porto Marghera. Riv. Geogr. Ital. 116, 445-465

US Army Environmental Center (USAEC). (2000). In-Situ Electrokinetic Remediation of Metal Contaminated Soils; Technology Status Report. Report Number: SFIM-AEC-ET-CR-99022

Villen–Guzman M., Paz–Garcia J.M., Jose M. Rodriguez-Maroto J.M., Garcia- Herruzo F., Amaya-Santos G., Gomez–Lahoz C., Vereda-Alonso C.(2015). Scaling-up the acid-enhanced electrokinetic remediation of a real contaminated soil. To appear in Electrochemial Acta.

Virkutyte J., Sillanpää M., Latostenmaa P. (2002). Electrokinetic soil remediation – critical overview. The Science of the Total Environment, 289, 97-121.

Volesky B., Holant Z.R. (1995). Biosorption of Heavy Metals. Biotechnol. Prog., 11, 235-250

Wang J., Feng X., Anderson C.W.N., Xing Y., Shang L. (2012). Remediation of Mercury contaminated sites – A review. Journal of Hazardous Materials 221, 1– 18

Wieczorek S., Weigand H., Schmid M., Marb C.(2005). Electrokinetic remediation of an electroplating site: design and scale-up for an in-situ application in the unsaturated zone. Engineering Geology 77, 203–215

Wu L., Long Z., Liu L., Qin Zhou Q., Lee Y., Zheng C. (2012). Microwave-enhanced cold vapor generation for speciation analysis of mercury by atomic fluorescence spectrometry. Talanta 94, 146-151

Wuana A.R. and Okieimen F. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. ISRN Ecology, Volume 2011, Article ID 402647

Yang X., Feng Y., He Z., Stoffella P.J. (2005). Molecular mechanisms of heavy metal hyperaccumulation and Phytoremediation. Journal of Trace Elements in Medicine and Biology 18, 339–353

Yao Z., Li J., Xie H., Yu C. (2012). Review on remediation technologies of soil contaminated by heavy metals. Procedia Environmental Sciences 16, 722–729

Yeung A.T., Gu Y. (2011). A review on techniques to enhance electrochemical remediation of contaminated soils. Journal of Hazardous Materials 195, 11– 29

Yukselen-Aksoy Y., Reddy K.R. (2012). Effect of soil composition on electrokinetically enhanced persulfate oxidation of polychlorobiphenyls. Electrochimica Acta 86, 164– 169

Web sites

Atlante della laguna: il geoportale della laguna, del territorio e della zona costiera di Venezia
http://www.atlantedellalaguna.it/

Regione del Veneto: Sistema Venezia, Stato avanzamenti degli interventi
http://sistemavenezia.regione.veneto.it/content/dati-ambientali-bonifiche

Ente zona industriale di Porto Marghera
http://www.entezona.it/

Toxnet: toxicology data network
http://toxnet.nlm.nih.gov/

Bosetti Gatti & partners:
http://www.bosettiegatti.eu/

Butti and partners:
http://www.buttiandpartners.com/

Regione Veneto: SIN Venezia Porto Marghera
http://www.regione.veneto.it/web/ambiente-e-territorio/sin-venezia-porto-marghera

R&C laboratory
http://www.rclabsrl.it/