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CHARACTERIZATION PLAN OF BORTOLOTTO LARGE AREA AND MULTI-TECHNIQUE APPROACH FOR THE STUDY OF THE THERMODYNAMIC AND SEQUESTERING PROPERTIES TOWARDS SOME TOXIC METALS OF LANDFILL LEACHATE FROM MUNICIPAL SOLID WASTE

PhD thesis of:
Chiara ALESSANDRELLO

Supervisor:
Prof. Francesco CREA

Coordinator:
Prof.ssa Concetta De Stefano

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1 Environmental pollutions

Pollution consists of the alteration or contamination of the environment by inorganic or organic agents (discharges, waste, etc.) or bacteria resulting from various human activities, whether productive or stationary. These agents can cause serious harm to human health and the living beings that inhabit the polluted environment. In the long term, this leads to a disruption of natural balances and environmental damage that can have devastating consequences.

The causes of pollution are manifold, but certainly anthropogenic causes are the most widespread and impactful, and they can be of chemical or physical origin.

1.1 Environmental pollutions: Types of pollution

There are different types of pollution:

- Natural pollution: Introduction of harmful substances into the environment due to natural events.
- Thermal pollution: Increase in the temperature of an environment due to natural or anthropogenic causes.
- Noise pollution: Introduction of sounds into the environment with decibel levels that exceed what the environment and its living organisms can tolerate without discomfort or harm.
- Electromagnetic pollution: Pollution caused by the presence of devices emitting electromagnetic fields.

Pollution can be associated with a single natural component (soil, water, and air) or can involve the entire ecosystem. However, due to hydrological cycles, if one component is contaminated, the others will also be affected by this damage.

1.2 Air Pollutions

Air pollution is the presence of harmful substances or solid particles suspended in the atmosphere. These substances, known as air pollutants, can come from various sources and have negative effects on human health, the environment, and the climate.

Sources of air pollution include:

- Vehicle emissions[1]: Motor vehicles, such as cars, trucks, and motorcycles, emit exhaust gases containing pollutants such as carbon monoxide (CO), nitrogen oxides (NOx), and hydrocarbons. These emissions can contribute to the accumulation of smog in urban areas and cause respiratory and cardiovascular problems in humans.

- Industrial emissions: Industrial activities, such as power plants, refineries, incinerators, and manufacturing industries, release a variety of chemical pollutants into the atmosphere, including sulphur dioxide (SO_2), nitrogen oxides (NO_x), fine particulate matter, and volatile organic compounds (VOCs). These emissions can contribute to the formation of industrial smog and can be harmful to human health and the surrounding environment.
- Fossil fuels: The combustion of coal, oil, and natural gas for energy production is a major source of air pollution. This process releases large amounts of CO_2, a greenhouse gas that contributes to global warming and climate change.
- Agricultural activities: Agriculture is responsible for greenhouse gas emissions such as methane (CH_4) and nitrous oxide (N_2O) from organic waste management, fertilizer production, and livestock digestion. These emissions contribute to the greenhouse effect and air pollution.

The effects of air pollution are varied and include health problems[2, 3] (respiratory issues such as asthma, chronic bronchitis, lung diseases, and allergies; increased risk of heart disease[4], stroke, and lung cancer), damage to terrestrial and aquatic ecosystems, with impacts on flora and fauna, and climate change caused by greenhouse gas emissions (these changes include rising global temperatures, altered precipitation patterns, rising sea levels, and increased extreme weather events such as storms, droughts, and heatwaves).

1.3 Soil pollution

Soil pollution occurs when the soil is contaminated by harmful or toxic substances, compromising its quality and its ability to support plant and animal life. This form of pollution is often caused by human activities and can have detrimental effects on human health, the environment, and agriculture.

There are several sources of soil pollution[5], including:

- Industrial discharge: Industrial activities often produce chemical and toxic waste that is disposed of in landfills or released directly into the soil. These substances can include heavy metals such as lead, mercury, and cadmium, as well as hazardous chemicals like solvents, hydrocarbons, and industrial chemicals. The accumulation of such substances can contaminate the soil and have a negative impact on the health of plants, animals, and humans.

- Solid waste: Improper disposal of solid waste, such as plastics, glass, metal, and household waste, can contribute to soil pollution. Waste that is not properly managed can release harmful chemicals into the soil and may take a long time to degrade.
- Use of pesticides and fertilizers: In intensive agriculture, the excessive use of chemical pesticides and fertilizers can cause soil pollution. These chemical products can accumulate in the soil, disrupt the balance of organisms in the soil, and affect soil quality. Additionally, they can pollute underlying water resources when washed away by rain.
- Oil and fuel spills: Accidents during the transportation or storage of oil and fuels can lead to spills that contaminate the surrounding soil. These substances can persist in the soil for a long time, causing significant damage to terrestrial ecosystems and agriculture.

Soil pollution can cause various issues[6, 7], including reduced soil fertility, leading to damage to agriculture and loss of biodiversity, contamination of water resources through leaching of pollutants from the soil, and inevitable impacts on human health (indirectly through ingestion of contaminated food grown in the soil, which can lead to poisoning, gastrointestinal diseases, neurological problems, and cancer).

1.4 Water pollution

Water pollution refers to the contamination of water resources such as rivers, lakes, groundwater, and oceans with harmful substances or excessive amounts of substances. It is a significant environmental issue that has serious consequences for human health, aquatic ecosystems, and biodiversity.

There are several sources of water pollution[8], including:

- Industrial discharges[9]: Industries often release toxic chemicals such as heavy metals, solvents, oils, and industrial chemicals into water bodies without proper treatment. These substances can be harmful to aquatic life and can accumulate in the food chain, causing damage to marine organisms and humans who consume contaminated fish.
- Urban discharges: Wastewater from urban communities, including domestic sewage and sewage systems, can contain pollutants such as bacteria, viruses, cleaning chemicals, and pharmaceuticals. If not treated properly, these wastewater discharges can contaminate

surrounding water resources, compromising the quality of drinking water and causing health problems.

- Agriculture[10]: The excessive use of chemical fertilizers and pesticides in agricultural activities can lead to soil erosion and the leaching of these substances into nearby water bodies. This can cause excessive algae growth in water, known as eutrophication, which depletes oxygen in the water and creates "dead zones" devoid of aquatic life.
- Oil spills: Oil spills during extraction, transportation, or fossil fuel consumption pose a significant risk of water resource pollution. These spills can cause damage to marine habitats, kill aquatic wildlife, and have long-term impacts on coastal ecosystems.

Water pollution has negative effects on the environment and human health[11-13]. Pollutants can make water unsafe to drink, cause gastrointestinal illnesses, damage the nervous system, and lead to developmental issues in children. Additionally, water pollution can destroy aquatic habitats, threaten the survival of native plant and animal species, and compromise overall biodiversity.

2 The Environmental Code

Legislative Decree No. 152 of April 3, 2006[14], commonly known as **Environmental Code**, is an Italian degree that collects the regulations regarding national environmental protection and consists of six parts, each addressing a specific aspect of environmental protection. Among these, we find the procedures for strategic environmental assessment (SEA), procedures for Environmental Impact Assessment (EIA), soil protection and combating desertification, water and air protection, and finally, it contains a section dedicated to regulations.

Legislative Decree 152/2006, whose structure is summarized in Table 1, is composed of six parts, each concerning a specific subject. In particular:

- **Part One - Common Provisions and General Principles:** includes articles 1 to 3-sexies and contains the common provisions and general principles of the six parts of the decree. The primary objectives are the safeguarding of the environment, improvement of environmental conditions, rational use of natural resources, and promotion of high levels of human quality of life.

- **Part Two - Procedures for Strategic Environmental Assessment (SEA), Environmental Impact Assessment (EIA), and Integrated Environmental Authorization (IPPC):** includes articles 4 to 52 and relates to the assessment of the impacts of plans, programs, and projects on the environment. This assessment aims to ensure that human activity is compatible with the conditions for sustainable development, using procedures for Strategic Environmental Assessment (SEA), Environmental Impact Assessment (EIA), and Integrated Environmental Authorization (IPPC).

- **Part Three - Regulations on soil protection, combating desertification, protection of water from pollution, and water resource management:** includes articles 53 to 176 and contains provisions aimed at ensuring the protection and restoration of soil and subsoil, prevention of hydrogeological disasters, and security measures for contaminated sites.

- **Part Four - Regulations on waste management and remediation of contaminated sites:** includes articles 177 to 266 and contains regulations for waste management and remediation of contaminated sites, providing measures to protect the environment and human health by avoiding or reducing waste production and negative impacts related to their production and management.

- **Part Five - Regulations on air protection and reduction of atmospheric emissions:** includes articles 267 to 298. This part presents regulations for air protection, particularly focused on the prevention and reduction of air pollution from thermal implants and activities that produce atmospheric emissions.

- **Part Six - Regulations on compensatory protection against damage to the Environment:** includes articles 298-bis to 318-octies and covers compensatory protection against damage to the environment. It also includes procedures for environmental prevention and restoration measures in cases where damages have not yet occurred.

Table 1: Structure of Legislative Decree 152/06

Structure of Legislative Decree 152/06
Part I- Common provisions and general principles
Part II- Procedures for SEA, EIA and IPPC
Part III- Regulations on soil protection, combating desertification, protection of water from pollution, and water resource management
Part IV- Regulations on waste management and remediation of contaminated sites
Part V- Regulations on air protection and reduction of atmospheric emissions
Part VI - Regulations on compensatory protection against damage to the Environment
Attachments

The fourth part of this decree will be discussed in detail in the following chapters, addressing regulations on landfills, measures for site characterization of contaminated sites, and remediation and safety procedures.

2.1 Definitions Art. 240

- **Site**: a geographically defined and determined area or portion of land, encompassing different environmental matrices (soil, including backfill materials, subsoil, and groundwater) and including any existing buildings and infrastructure.
- **Contamination threshold concentrations (CSC)**: the contamination levels of environmental matrices that exceed values requiring site characterization and site-specific risk analysis, as identified in Annex 5 to the fourth part of this decree. In cases where a potentially contaminated site is located in an area affected by anthropic or natural phenomena that have resulted in the exceeding of one or more contamination threshold concentrations, these values are assumed to be equal to the existing background value for all exceeded parameters.
- **Risk threshold concentrations (CSR)**: the contamination levels of environmental matrices, to be determined on a case-by-case basis through the application of a site-specific risk analysis procedure based on the principles outlined in Annex 1 to the fourth part of D. Lgs 152/06 and the results of the characterization plan. Exceeding these concentration levels requires remediation and security measures. The defined concentration levels constitute the acceptability levels for the site.
- **Potentially contaminated site:** a site where one or more concentrations of pollutants detected in the environmental matrices exceed the contamination threshold concentrations (CSC), pending the completion of site characterization and site-specific health and environmental risk analysis to determine the presence or absence of contamination based on the risk threshold concentrations (CSR).
- **Contaminated site**: a site where the values of the risk threshold concentrations (CSR), determined through the application of the risk analysis procedure described in Annex 1 to the fourth part of this decree based on the results of the characterization plan, are exceeded.
- **Non-contaminated site**: a site where the contamination detected in the environmental matrices is below the contamination threshold concentrations (CSC) or, if higher, still lower than the risk threshold concentrations (CSR) determined through site-specific health and environmental risk analysis.
- **Site with ongoing activities**: a site where productive activities, both industrial and commercial, are being carried out, including neighbouring areas and those used for ancillary

economic activities, including maintenance and protection activities for the purpose of future resumption of activities.

- **Abandoned site**: a site where productive activities have ceased.
- **Prevention measures**: initiatives aimed at countering an event, act, or omission that has created an imminent threat to health or the environment, understood as a reasonably probable risk of future damage to health or the environment, in order to prevent or minimize the occurrence of such a threat.
- **Remediation measures**: any action or combination of actions, including mitigation or interim measures aimed at repairing, restoring, or replacing damaged natural resources and/or natural services, or providing an equivalent alternative to such resources or services.
- **Emergency security measures**: immediate or short-term interventions to be carried out under emergency conditions, in the case of sudden contamination events of any nature, intended to contain the spread of primary sources of contamination, prevent their contact with other matrices present on the site, and remove them, pending any further remediation or permanent safety measures.
- **Operational security measures**: the set of interventions carried out on a site with ongoing activities to ensure an adequate level of safety for people and the environment, pending further measures for permanent security or remediation to be implemented upon cessation of activities. These measures also include interventions to contain contamination temporarily until the execution of remediation or permanent security measures, in order to prevent the spread of contamination within the same matrix or between different matrices. In such cases, appropriate monitoring and control plans must be prepared to verify the effectiveness of the adopted solutions.
- **Permanent security measures**: the set of interventions aimed at definitively isolating pollutant sources from the surrounding environmental matrices and ensuring a high and permanent level of safety for people and the environment. In these cases, monitoring and control plans and usage restrictions must be established in accordance with urban planning provisions.
- **Remediation**: the set of interventions aimed at eliminating pollution sources and pollutants or reducing their concentrations in soil, subsoil, and groundwater to a level equal to or below the risk threshold concentrations (CSR).

- **Restoration and environmental restoration:** environmental and landscape requalification interventions, which may also complement remediation or permanent security measures, aimed at restoring the site for effective and definitive use in accordance with urban planning provisions.
- **Diffuse pollution**: contamination or chemical, physical, or biological alterations of environmental matrices resulting from diffuse sources that cannot be attributed to a single origin.
- **Site-specific health and environmental risk analysis**: site-specific analysis of the effects on human health resulting from prolonged exposure to substances present in contaminated environmental matrices, conducted in accordance with the criteria indicated in Annex 1 to the fourth part of this decree.
- **Emergency conditions**: events that require emergency interventions, such as:
- 1) Current or potential concentrations of vapours in confined spaces near explosivity levels or capable of causing acute health hazards.
- 2) Significant presence of separated-phase products in soil, surface water, or aquifers.
- 3) Contamination of drinking water wells or wells used for agricultural purposes.
- 4) Fire and explosion hazards.

3 Waste Disposal

Waste, as per the definition, is "any substance that the holder intends to get rid of or is obliged to get rid of, or any substance or object resulting from human activities or natural processes that is abandoned or intended to be abandoned."

The production and disposal of waste are pressing issues today. Not only do wastes represent the consumption of non-renewable natural resources that are not replenished or reintroduced into the production cycle, but their storage also poses a burden in terms of expenses and potential sources of contamination.

In Italy, the situation is challenging, especially due to the presence of inadequate landfills constructed before the current legislation (which will be discussed later) was approved. The growing interest in the circular economy and the reuse of raw materials, as well as the new provisions implemented by the government regarding recycling (Legislative Decree of September 3, 2020, No. 121[15], implementing Directive (EU) 2018/850[16] amending Directive 1999/31/EC[17] on landfill sites), are leading to a modification of the simple collection/storage system as defined in the new Article 1.

"*Article 1 (Purpose). - 1. This decree ensures a progressive reduction in landfilling of waste, particularly those suitable for recycling or other types of recovery, in order to support the transition to a circular economy and comply with the requirements of Articles 179 and 182 of Legislative Decree April 3, 2006, No. 152, and to provide, through operational and technical requirements for waste and landfills, measures, procedures, and guidelines aimed at preventing or minimizing as much as possible the negative impacts on the environment, particularly pollution of surface waters, groundwater, soil, and air, on the agri-food and cultural heritage, and landscape, and on the global environment, including the greenhouse effect, as well as the risks to human health resulting from waste landfills throughout the entire lifecycle of the landfill.*"

According to recent studies published by Istat[18], the separate collection of urban waste has increased from 9.4% in 1997 to 63% in 2020. As for the recycling of industrial waste, there has been an increase of nearly 50 percentage points: from 21% in 1997 to 70% in 2020.

Nevertheless, it is necessary to ensure the proper landfill disposal of non-recyclable waste and to pay special attention to storage in order to avoid possible environmental contamination resulting from issues related to adequate waste storage.

3.1 Current Legislation

Among the main Italian legislative instruments in the field of waste, the **Decree of February 5, 1997, No. 22 (Ronchi Decree) [19]** stands out. It implements Directives 91/156/EEC on waste, 91/689/EEC on hazardous waste, and 94/62/EC on packaging and packaging waste. It defines the definitions and classifications of waste, the responsibilities of the State, Regions, Provinces, and Municipalities, as well as the identification of various types of waste in the annexes.

This Decree is associated with the **Legislative Decree of January 13, 2003, No. 36[20],** which implements Directive 1999/31/EC on landfill sites. It was updated in 2020 according to **Legislative Decree of September 3, 2020, No. 121[15]**, implementing Directive (EU) 2018/850[16] ,amending Directive 1999/31/EC[17] on landfill sites.

The classification of waste is the first step towards proper disposal and can be carried out in various ways. According to Legislative Decree 152/06, Article 184:

1. For the implementation of the fourth part of this decree, waste is classified, according to its origin, as urban waste, and special waste, and, according to its hazardous characteristics, as hazardous waste and non-hazardous waste.

2. Urban waste includes:

a) Household waste, including bulky waste, from premises used for residential purposes.

b) Non-hazardous waste from premises used for purposes other than those mentioned in point (a), assimilated to urban waste in terms of quantity and quality, according to Article 198, paragraph 2, point (g).

c) Waste resulting from street sweeping.

d) Waste of any nature or origin lying on public roads or areas, or on private roads or areas open to public access, or on coastal and lakeside beaches, or on the banks of watercourses.

e) Vegetative waste from green areas, such as gardens, parks, and cemeteries.

f) Waste resulting from exhumations and disinterments, as well as other waste from cemetery activities, excluding those mentioned in points (b), (c), and (e).

3. Special waste includes:

a) Waste from agricultural and agro-industrial activities, according to Article 2135 of the Civil Code.

b) Waste resulting from demolition and construction activities, as well as waste resulting from excavation activities, without prejudice to the provisions of Article 184-bis.

c) Waste from industrial processes.

d) Waste from artisanal processes.

e) Waste from commercial activities.

f) Waste from service activities.

g) Waste resulting from waste recovery and disposal activities, sludges produced from water treatment and other treatment of waters, and sludges from flue gas treatment.

h) Waste resulting from healthcare activities.

Of particular interest is the Legislative Decree of January 13, 2003, No. 36, which establishes the rules for implementing Directive 1999/31/EC on landfill sites. It defines the technical aspects for the classification and construction of landfills. In particular, Article 4 deals with landfill classification, stating:

a) Inert waste landfill.

b) Non-hazardous waste landfill.

c) Hazardous waste landfill.

A detailed explanation of the eligible waste for landfill disposal is provided in Article 7, stating that waste can only be disposed of in a landfill after treatment to reduce waste quantity or limit risks to human health and the environment. If treatment is unnecessary or redundant to achieve what is stated in Article 1, no treatment is carried out, and the waste is disposed of as is.

Landfills for non-hazardous waste accept urban waste (referred to as MSW), and Directive 1999/31/EC states that only materials with low organic carbon content and non-recyclable materials are allowed in landfills. It is prohibited to dispose of waste that can be recycled or materials suitable for composting in this manner. Recycling and composting remain the primary strategies for waste disposal. This is due to the fact that residues from many wastes, especially organic urban waste, remain active even beyond 30 years due to natural anaerobic decomposition processes, producing biogas and various liquid residues (leachate), which can be hazardous pollutants for soil and groundwater.

In the next chapter, different types of landfill facilities and proper waste disposal according to current regulations will be explained.

3.2 Landfills for MSW and landfill Leachate

According to the definition provided in Annex B (Item D1) of the Fourth Part of the Legislative Decree 152/2006, a landfill refers to a disposal operation that involves the "deposit on or into the ground" of waste, either permanently or with a tendency to be so.

The same legislation has recently been updated with Legislative Decree 121/2021, which has implemented landfill management procedures and a surveillance plan. It requires periodic monitoring of chemical, physico-chemical, hydrogeological, meteorological, climatic, and topographic parameters at predetermined intervals. Since materials with significant degradation times (such as plastics or hazardous waste) were disposed of until a few years ago, it is reasonable to expect traces of such substances to be detectable for decades, if not centuries, after the closure of a landfill. All of this could be avoided with a different waste storage and pre-treatment plan.

Regarding the greenhouse gases emitted into the atmosphere and responsible for climate change, it has been scientifically proven by the Intergovernmental Panel on Climate Change (IPCC) that landfill waste causes high emissions of methane and carbon dioxide, both potent greenhouse gases. The provisions for the proper construction of a landfill to mitigate these emissions include the installation of adequate gas collection systems, especially for methane, which can be reused as an energy source. Furthermore, emission issues can be reduced or eliminated at the source by employing specific construction techniques and pre-treatment of waste (such as separate collection of the organic fraction responsible to produce liquid and gaseous products and the so-called cold treatment, which accelerates waste decomposition before landfill disposal).

Regarding the construction process, a landfill involves the final storage of waste in overlapping layers, promoting the fermentation of organic matter and limiting the flow of pollutants to the outside. The decomposition processes of organic substances are carried out by anaerobic bacteria present in the landfill, leading to the production of landfill leachate and biogas. A legally compliant landfill incorporates a collection system for both leachate and biogas to prevent soil, surface water, groundwater, and air pollution. Impermeable barriers are installed at the bottom and walls of the landfill, and drainage systems for leachate and wells for biogas collection are constructed. Other challenges in the proper construction of a landfill include waste stability and settling conditions, stability issues of the supporting ground, slopes, and containment structures (berms). Finally, activities for the closure of the facility and the recovery of the landfill area must be planned. Designing a landfill, therefore, requires interdisciplinary cooperation involving various professionals to consider all the necessary aspects for proper implementation, including geotechnical, hydraulic, chemical, and regulatory considerations.

In general, three types of landfills are constructed based on the hydrological and geomorphological characteristics of the site:

- Valley landfills (or trench landfills): These are created by filling old abandoned quarries or specially excavated "pits" in the ground.
- Raised landfills: They are situated at ground level and develop in height.
- Slope landfills: These are constructed adjacent to slopes to fill gaps along the slopes caused by quarries, landslide-prone areas, or catchment areas (Figure 2).

The schematic representation of the different types of landfills is shown below (Figure 1):

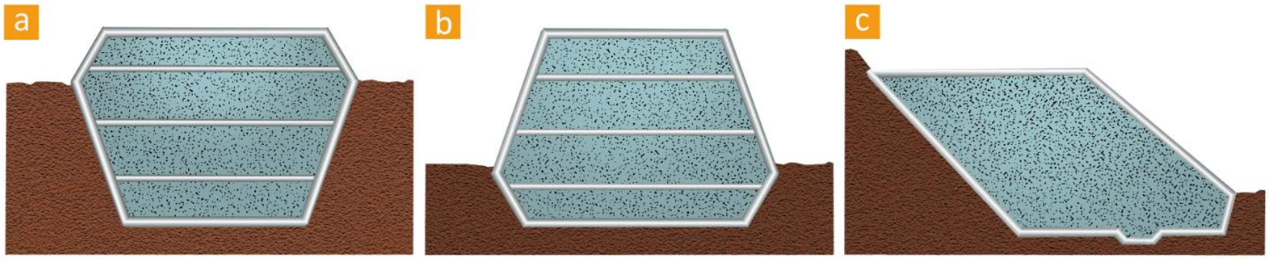


Figure 1: (a) Valley landfill; (b) raised landfill; (c) slope landfill.

Figure 2: A slope landfill

The choice of the construction site for a landfill is not random and must comply with specific characteristics.

Landfills for hazardous and non-hazardous waste should not be located in the following areas:

•In active fault zones and areas affected by volcanic activity, as it would compromise the stability of the facility.

•In sinkholes, swallow holes, or other forms of surface karst phenomena.

•In areas where surface geomorphological processes such as accelerated erosion, landslides, slope instability, or river channel migration could jeopardize the integrity of the landfill and its associated structures.

•In areas subject to hydrothermal activity.

•In flood-prone or unstable areas.

In the planning of a landfill, consideration should also be given to the byproducts generated from the biodegradation of waste: biogas and leachate. To prevent the uncontrolled release of these byproducts, it is necessary to implement a system that contains their escape. In this regard, the presence of low-permeability barriers is required .

These barriers can be natural, consisting of soil layers containing clay that may already be present naturally or intentionally placed and compacted. More commonly, artificial barriers or geomembranes are used (Figure 3).

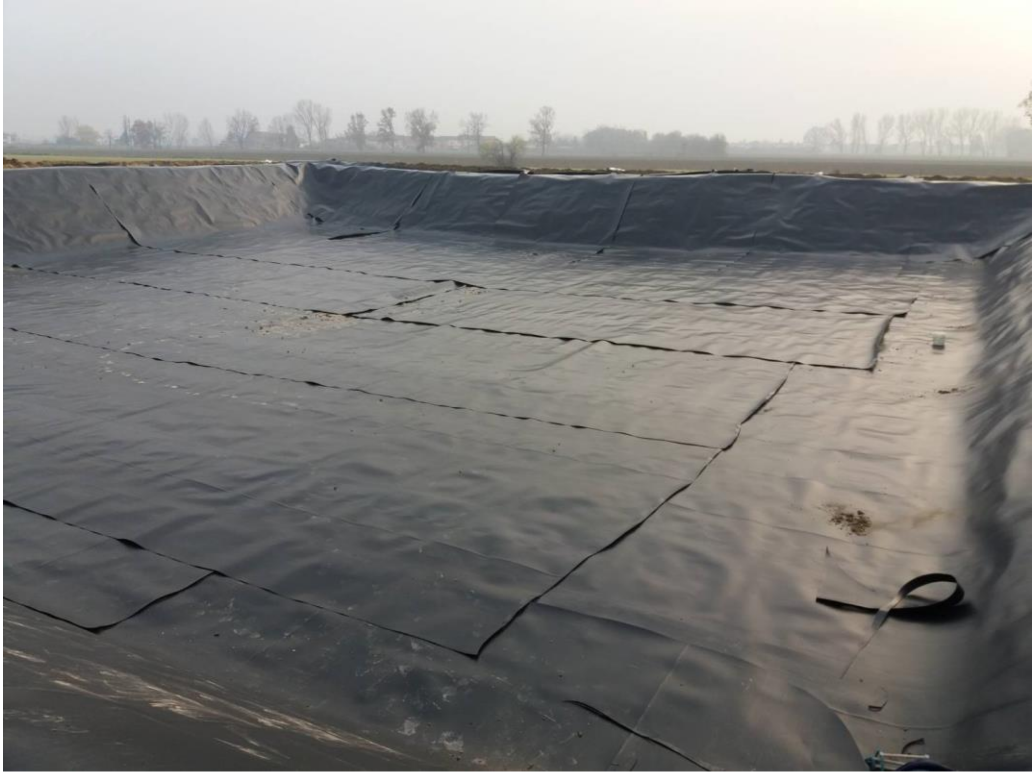


Figure 3: An example of an artificial geomembrane

The new Legislative Decree No. 121/2020, which amends Directive 1999/31/EC on waste landfills, defines the physical parameters that natural barriers must comply with and establishes the necessary combination of natural and artificial barriers if these parameters are not met.

Another aspect to consider is the potential presence of underground aquifers; the water table must be at least 1.5 meters below the base level of the barrier.

Lastly, the barrier must also extend along the lateral sides of the landfill to prevent any leakage of biogas or leachate into the surrounding soil, which may laterally infiltrate the waste mass.

To ensure compliance with the minimum parameters, all components of the system undergo thorough investigations.

Landfills for municipal solid waste have a collection and removal system for the leachate generated during the biodegradation processes. It is collected in pockets between different layers of stored waste, and if not adequately collected, it tends to accumulate at the bottom or overflow from the lateral edges.

Leachate collection pipes are positioned in a drainage layer between the waste and the impermeable bottom barrier to capture the liquid and convey it to a collection sump. From the collection sump, the leachate is pumped into a settling tank, from which it is sent to a treatment plant, which can be either internal or external.

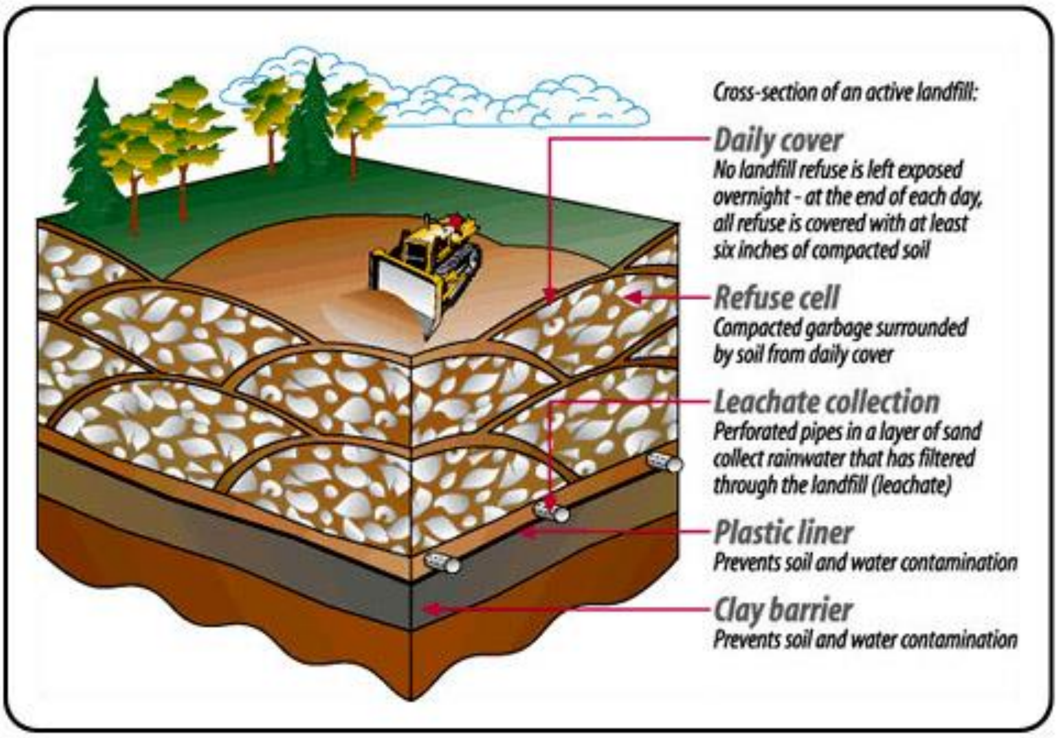


Figure 4: Layered waste system of a landfill with highlighted leachate collection system.

If the landfill is completely isolated, in addition to the accumulation of leachate, there is also the accumulation of biogas. Biogas mainly consists of methane and carbon dioxide, both greenhouse gases. Methane is also explosive and odorous. To avoid the consequences of possible air or subsurface dispersion and damage to the surrounding areas from both an environmental and human perspective, it is necessary to provide a dedicated collection system.

The extraction system consists of a series of perforated pipes that are horizontally placed within the waste body to cover the entire site and reach a series of vertical wells to reach the surface. The system utilizes the pressure to which the gases inside the waste are subjected, allowing for their collection and removal. The extraction can be either natural or forced.

The collected biogas can undergo two treatments depending on the size of the landfill:

1 It can be directed to a combustion flare for disposal (for small landfills where biogas production is limited).

2 It can be reused as fuel to self-power the landfill itself (for large landfills) as shown in Figure 5.

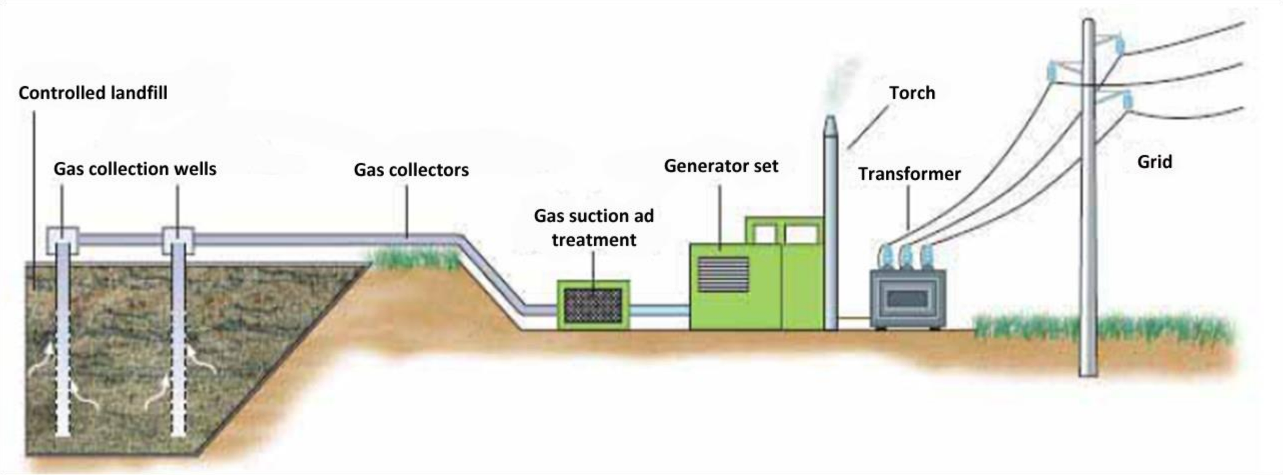


Figure 5: Methane reuse from landfill as an energy source

The "life" of a landfill does not end when waste is no longer deposited, but three important objectives must be considered:

a. Reduction of surface rainwater infiltration to contain leachate production.

b. Control of biogas emissions into the atmosphere.

c. Green recovery of the area.

Regarding the first point, during landfill management, a surface barrier is applied after each day of waste deposition to isolate the waste and prevent the infiltration of surface rainwater, as shown in

Figure 4. During the closure phase of the facility, a final cover is then applied to completely seal the entire basin, preventing an increase in the volume of leachate, especially during periods of high rainfall. Rainwater must be channeled through appropriate runoff channels and diverted away from the site. Normal settlement movements within the landfill body must also be considered in relation to the overall structure of the facility.

For the second point, similar considerations apply: the final surface cover aims to contain gas dispersion and prevent both its harmful effects and the release of unpleasant odors. In this case as well, the collection system, even during the post-management phase, must remain active as long as biogas production is present.

Green recovery of the area is achieved through vegetative cover of the landfill body. The choice of vegetation should be based on site-specific characteristics, taking into account local climatic conditions and the selected plant species. Adequate nutrients should be added, and pH should be regulated based on the evaporation of the slightly basic leachate (to prevent plant species from dying due to unfavourable growth conditions).

Factors that can lead to the death of planted species cannot be completely excluded and include soil immaturity, irregular water drainage, and root suffocation due to gas leakage from the extraction system.

The hydrogeological cycle of a landfill is a significant factor as it is not completely interrupted but rather altered. It is therefore necessary to consider that a small portion of the leachate may filter into the soil, and the lining systems must be appropriately sized. A diagram of a controlled landfill is provided in Figure 6.

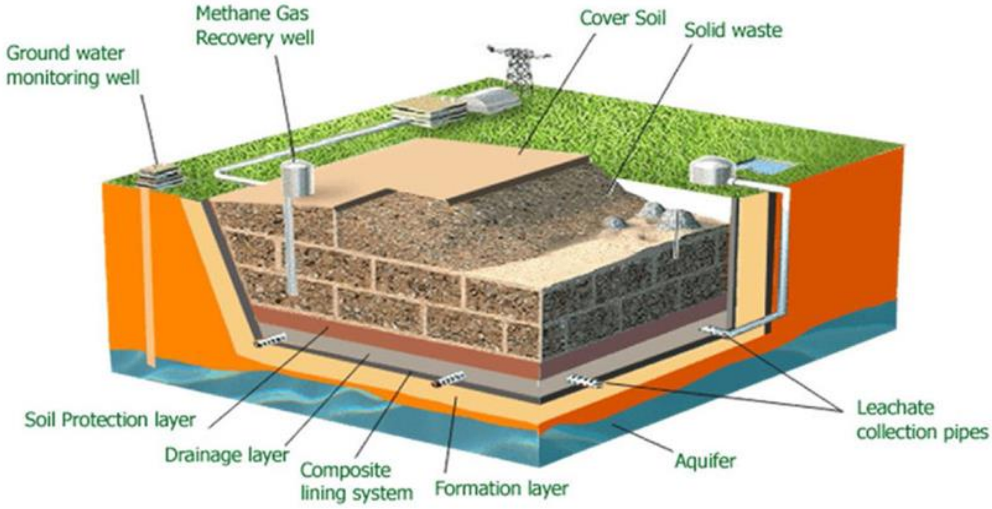


Figure 6: Diagram of the various parts and phases that make up a controlled landfill.

3.3 Hydrological balance of a landfill

Estimating the production of leachate in a landfill is not possible through precise mathematical models but is typically based on simple empirical expressions of balance. Solving the balance equation involves analytically expressing each of the parameters that appear in it. The results applied to a real system are very accurate in modelling the phenomenon of percolation during the post-closure phase but are not as accurate during the operational phase due to the inability to consider all the variables involved.

During the post-closure phase, where physical and geometric parameters are constant and well-defined, more realistic estimates can be made. In contrast, during the operational phase, the waste deposition methods constantly modify the aforementioned parameters. Therefore, it is possible to choose a stochastic approach to studying leachate production in a landfill, considering the factors that contribute to and influence the hydrological balance as random variables. The most appropriate method would be to assess the reciprocal influences, in probabilistic terms, of the observed values and then focus on studying the joint probability distribution of the chosen system of random variables. Among the analysis methods, computer-implemented numerical models with specific programs, such as the HELP code developed by the EPA[21], are increasingly used. Two widely used numerical models that simulate leachate production in active landfills are the Deterministic Multiple Linear Reservoir Model (DMLRM) and the Stochastic Multiple Linear Reservoir Model (SMLRM), developed by researchers from the University of Florida.

In the next paragraph, the data to be considered, which are part of the hydrological cycle of a landfill, will be explained in detail.

3.3.1 Components of the hydrological cycle

The starting point for a hydrological balance is precipitation (averages or for a specific period of time, estimated based on recorded data near the site). This data is then broken down into various components of the hydrological balance (expressed as percentages of the total precipitation value), which correspond to different phenomena that contribute to determining the water flow at the site under consideration.When meteoric water reaches the surface, taking into account irrigation water and surface runoff, it can follow different paths:

1. A portion of the water is retained by the vegetation present on the surface and subsequently evaporates.

2. In colder climates, water may temporarily accumulate on the surface as snow or ice and then melt and evaporate.
3. Some of the water is diverted away from the landfill by flowing along the surface of the cover to drainage channels.
4. The remaining portion infiltrates into the soil.

Considering the last fraction, the water can:

1. Be returned to the atmosphere through plant roots via evapotranspiration (ET).
2. Evaporate and directly reach the atmosphere.
3. Percolate through the cover soil, below the evapotranspiration zone, forming a layer between this zone and the lining barrier.

The water in this layer:

- Is retained by the impermeable barrier, if present.
- Is collected by the drainage system, if present.
- Reaches the waste.

If the water reaches the waste, it can either be absorbed by the waste (waste moisture) or be released and correspond to the leachate. Figure 7 represent a schematic representation of the hydrological cycle of a controlled landfill.

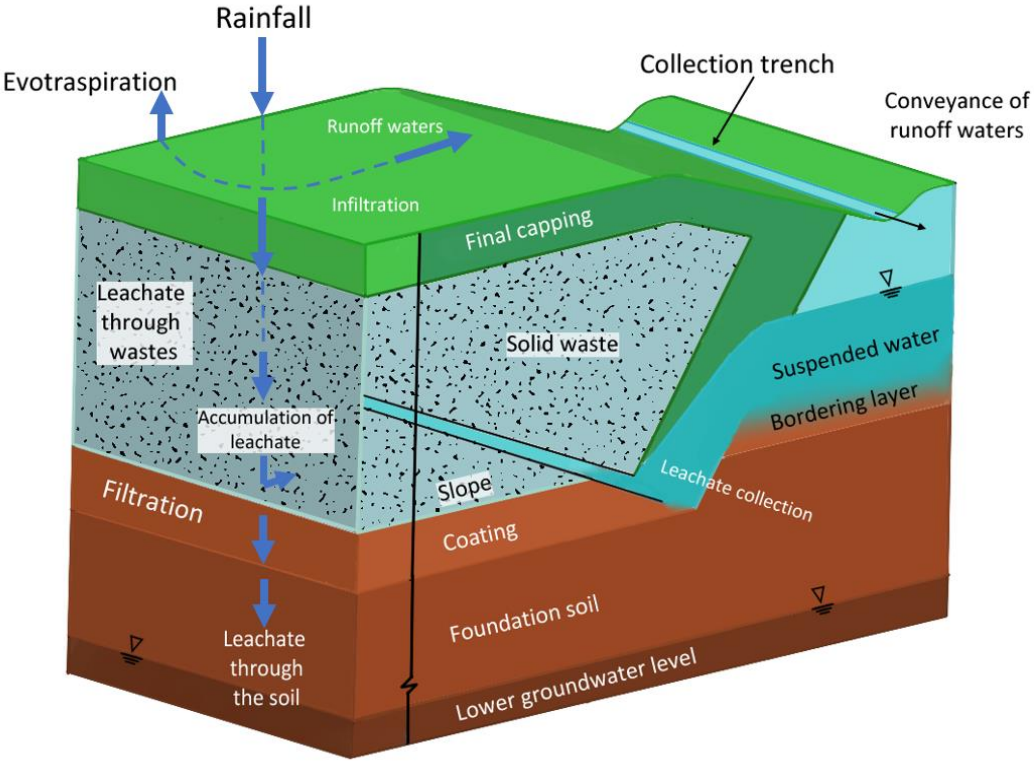


Figure 7: Hydrological cycle in a controlled landfill

3.4 Leachate

Leachate is defined as the liquid generated in a landfill from the interaction of decomposition products with infiltrated meteoric water within the waste mass.

According to Article 2, point m) of Legislative Decree 13 January 2003, no. 36 "Implementation of Directive 1999/31/EC on the landfill of waste" published in the Official Gazette no. 59 on 12 March 2003 - Supplement no. 40[20], leachate is defined as: "liquid originating mainly from water infiltration into the waste mass or from their decomposition."

When deposited, the organic matter present in the waste undergoes biodegradation processes carried out by preexisting bacterial flora, whose times vary depending on the nature of the compounds present. The biochemical reactions are initially aerobic due to the initial presence of oxygen in the waste, which is trapped during disposal. When the oxygen is completely consumed, as seen earlier, in a closed system, the reactions proceed anaerobically. The rate of the processes initially increases to a constant value and then gradually decreases due to the progressive reduction of the more easily biodegradable products.

The processes require the involvement of multiple bacterial groups in a sequential manner, each of which is crucial for the activity of the remaining groups. The olfactory and visual characteristics of the leachate vary depending on the age of the landfill. Initially, the leachate assumes yellow-green coloration and then becomes brownish-black(Figure 8).

Figure 8: Different leachate samples

The characteristic odor of young landfills (2 or 3 years old) is derived from hydrogen sulphide, while in older landfills, the smell of mold prevails. The pollutant load also varies, with a peak in the early years of the landfill's life and gradually decreasing over time.

The mechanisms that determine the production of leachate (transfer of solid matter to percolating water) are as follows:

1. Hydrolysis of suspended and dissolved organic compounds, facilitated by extracellular enzymes produced by fermentative bacteria. This phase is of considerable importance as it serves to make a significant portion of the organic matter available. It alternates between an aerobic degradation phase (limited by the amount of present oxygen), resulting in the production of carbon dioxide, water, alkanes, and volatile acids, and an anaerobic phase that lowers the pH and leads to the formation of carbon dioxide and methane.
2. Solubilization of salts.
3. Leaching of matter: soluble elements migrate to deeper layers due to water, which, by gravity, passes through the waste and flows towards the bottom of the landfill.

Regarding the interactions between different substrates and bacterial groups, a list of sequential digestion processes can be defined[22] (Christensen and Kjedsen, 1989):

a) Hydrolysis of suspended organic compounds and dissolved ones; fermentative bacteria make the organic matter available.
b) Acidogenesis, predominantly facultative bacteria transform the organic matter into volatile fatty acids, alcohols, hydrogen, and carbon dioxide.
c) Acetogenesis, facultative bacteria transform fatty acids and alcohols into acetic acid, hydrogen, and carbon dioxide.
d) Methanogenesis, anaerobic acetoclastic methanogenic bacteria produce methane from either the acetic acid produced in the previous phase or from hydrogen and carbon dioxide.
e) Sulphate reduction, in this phase, obligate anaerobic bacteria (known as sulphate-reducers) transform acetic acid and fatty acids, utilizing the available hydrogen, into hydrogen sulphide and carbon dioxide.

The following image schematizes the above information.

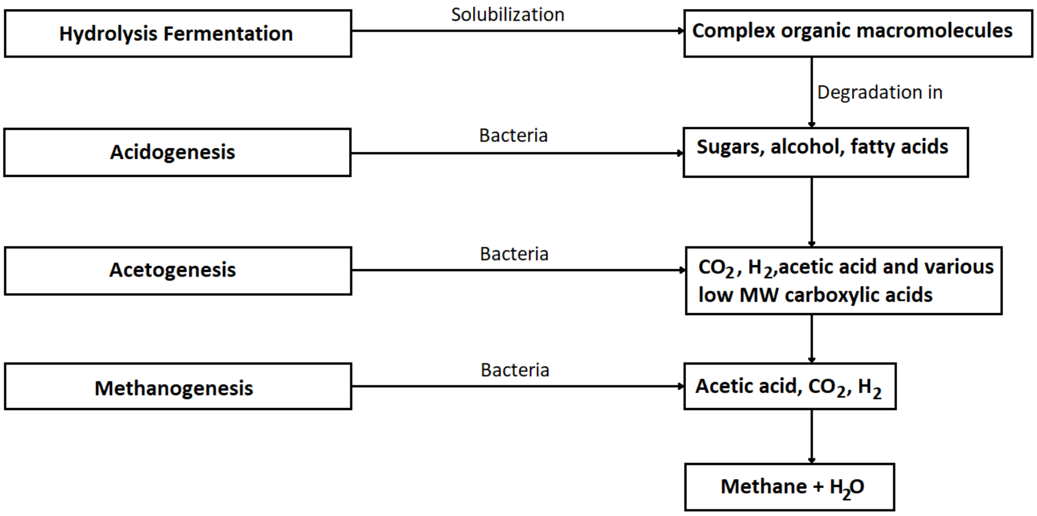


Figure 9: Scheme of the leachate digestion process

Considering the stages of the described anaerobic process, taking a unit sample of waste into account, it is possible to identify five phases of the degradation process from the moment the waste is deposited[23] [22] (Augestein and Pacey, 1991; Christensen and Kjedsen, 1989):

- Phase I (aerobic fermentation):

Occurs immediately after the waste is landfilled, due to its initial air content. It lasts from a few hours to a few days, depending on the initial porosity of the waste and the compaction methods used.

During this initial phase, proteins are degraded into amino acids, then into carbon dioxide, water, nitrates, and sulphates. Carbohydrates are converted into carbon dioxide and water, and fats are hydrolysed into fatty acids and glycerol. Therefore, the result of hydrolysis is the solubilization of materials into sugars, alcohols, and long chains of fatty acids, reducing the size of organic molecules and enabling their transport across microbial cell membranes.

Cellulose, which constitutes the predominant part of the organic fraction of the waste, is degraded into glucose, which is subsequently utilized by bacteria and converted into CO_2 and H_2O.

$$(C_6H_{10}O_5)_n + n\ H_2O \rightarrow n\ C_6H_{12}O_6$$

This stage, due to the exothermic nature of biological oxidation reactions, is characterized by reaching high temperatures (60-70 °C). The increase in partial pressure of carbon dioxide, which dissolves in water forming a weak acid, not only lowers the pH but can also dissolve other mineral substances. As a result, the leachate formed in this initial phase is slightly acidic and typically maintains a high COD content, also due to the presence of partially degraded organic substances. However, it should be noted that during this initial decomposition phase, the quantities of leachate produced are minimal, as the waste has not yet reached hydrological stabilization, and the process tends to absorb the liquids present.

- Phase II (acidic fermentation, anaerobic):

Once oxygen is depleted, biodegradation processes such as anaerobic respiration begin. In this phase, oxidized inorganic compounds (nitrates and sulphates) can be used as a source of oxygen. The exothermic nature of the reaction is less pronounced than in the previous stage. A wide variety of products can form from the initial organic substrate, which typically consists of fatty acids, sugars, and amino acids. Volatile organic acids such as acetic, propionic, and butyric acids can be formed from glucose, as described in the following reactions. These acids, along with the dissolved carbon dioxide, whose formation continues to increase, accentuate the acidic properties of the percolate, which generally has a pH ranging from 5.5 to 6.5. The activity of fermentative and acetogenic bacteria results in the transformation of biodegradable substances into volatile acids (low molecular weight fatty acids), carbon dioxide, and hydrogen, leading to a decrease in pH. The high concentrations of fatty acids result in high COD values (Chemical Oxygen Demand). This phase lasts several months.

$C_6H_{12}O_6 \rightarrow CH_3(CH_2)_2COOH + 2\ H_2 + 2\ CO_2$

$C_6H_{12}O_6 + 2\ H_2 \rightarrow 2\ CH_3CH_2COOH + 2\ H_2O$

$C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COOH + 4\ H_2 + 2\ CO_2$

Unlike aerobic metabolism, where the conversion of organic matter is almost always carried out by a single species of bacteria, anaerobic metabolism requires different types of bacterial populations, each of which partially oxidizes a specific class of compounds. These first two phases are completed within a timeframe of 5-7 months.

- Phase III (methanogenic fermentation, unstable, anaerobic):

In this phase, the anaerobic methanogenic decomposition process begins, during which methanogens, a highly heterogeneous bacterial class, convert partially degraded organic matter into CH_4 and CO_2. During this phase, the long chains of volatile fatty acids are converted into acetic acid.

$CH_3(CH_2)_2COOH + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ H_2$

$CH_3CH_2COOH + 2\ H_2O \rightarrow CH_3COOH + 3\ H_2 + CO_2$

As a result of the consumption of organic acids, the COD concentration in the leachate decreases, and its pH increases, approaching neutrality. This behaviour leads to a reduction in the chemical aggressiveness of the leachate and a decrease in the concentrations of inorganic compounds (due to the pH's influence on solubility). Following the consumption of soluble substrates, methane production from waste becomes dependent on the hydrolysis of cellulose, which contains the highest amount of effectively biogasifiable carbon. The percentage of methane in the gas mixture progressively increases, leading to a decrease in the partial pressure of carbon dioxide. This third phase, characterized by the progressive increase in the volumetric fraction of methane, lasts for a period ranging from a few months to 2-3 years.

- Phase IV (methanogenic fermentation, stable, anaerobic):

The anaerobic transformation process of biodegradable organic matter reaches equilibrium with constant volumetric fractions of methane and carbon dioxide. The following equations summarize the functions carried out by methanogens.

$CH_3COOH \rightarrow CH_4 + CO_2$

$4\ H_2 + CO_2 \rightarrow CH_4 + H_2O$

The percentage of methane is quite variable but falls within a range of 45-65%. The progressive development of the methanogenic population leads to an increase in the amount of methane produced, reaching a stable value of 50-65% of the biogas produced, with the remaining portion mainly consisting of CO_2. This phase lasts for several years (from 8 to 40 years).

- Phase V (exhaustion phase):

The gradual stabilization of the waste results in the availability of less biodegradable organic compounds over time. The reduction in bacterial activity, and therefore biogas production, leads to the diffusion of air within the waste, resulting in the presence of oxygen and nitrogen in the upper layers. This phase lasts from 10 to 80 years.

The mechanisms of pollutant transfer to the leachate have been studied by various authors[24] (Qasim and Burchinal, 1970) and can be summarized into three phases:

1 The first phase, lasting a few days, involves a progressive increase in waste moisture until reaching field capacity. Pollutants are desorbed from the solid phase (waste) into the liquid phase (leachate).

2 During the second phase, lasting several weeks, there is a progressive increase in the amount of leachate produced, and the dilution phenomenon prevails over desorption, although it diminishes due to the increasing concentration of the adsorbing liquid.

3 The third phase involves the degradation of organic matter present in the waste, initially through aerobic and subsequently anaerobic processes, as well as leaching processes. This phase initially shows increasing trends followed by an exhaustion phase.

Therefore, the quality of the leachate[25] varies significantly depending on the stabilization phase during which it is produced. Neglecting the brief aerobic phase, in the acidic phase, the presence of volatile acids results in highly polluted leachate with very high COD concentrations, reaching up to 100,000 mg/l. In this phase, the BOD/COD ratio is around 0.5-0.7, and the low pH favours the solubilization of metals. In the subsequent methanogenic phase, the pollution level reduces, with BOD values reaching 100-200 mg/l over approximately 10 years. In this phase, the BOD/COD ratio decreases to values close to 0.1 due to the reduced biodegradability of the waste.

As a result, the highest pollutant loads occur during the early years of landfill management. After approximately 2-3 years, there is a progressive decrease in the values of organic pollution parameters (TOC, COD, BOD), microbiological parameters, and major inorganic ions. The variability of the physico-chemical parameters of the leachate depends on various factors, including: i) differences in the age of waste in the landfill and the stage of biostabilization; ii) different meteorological and climatic conditions at the landfill sites; iii) different landfill management practices. In a publication by Ehrig, [26] (Ehrig. H.J., "Water and Element Balances of Landfills", in Lecture Notes in Earth Sciences, The Landfill, P. Baccini, editor. p. 83-115, Springer-Verlag Press, 175 Fifth Avenue, New York, NY 100910 (1989)), a table derived from an analysis of literature data on leachate from different landfills is presented, indicating the ranges of physico-chemical parameters during both the acidic and methanogenic phases. Information from this table is reported in Table 2.

Table 2: Range of oscillation of characteristic parameters of leachate during the acidic and methanogenic phases.

Parameter	Unit of measurement	Acidic phase		Methanogenic phase	
		Min	Max	Min	Max
pH		4.5	7.5	7.5	9
COD	mg O_2/l	6000	60000	500	4500
BOD_5	mg O_2/l	4000	40000	20	550
Sulphates	mg/l	70	1750	10	420
Calcium	mg/l	10	2500	20	600
Magnesium	mg/l	50	1150	40	350
Iron	mg/l	20	2100	3	280
Manganese	mg/l	0.3	65	0.03	45
Zinc	mg/l	0.1	120	0.03	4
Strontium	mg/l	0.5	15	0.3	7

It is evident that the transition from the acidic phase to the methanogenic phase leads to an increase in pH and a consequent decrease in parameters such as BOD_5 and COD. Simultaneously, there is a decrease in organic load and a reduction in the concentration of "heavy" metals in solution.

For many other chemical and physico-chemical parameters, there is no significant concentration trend observed between the acidic and methanogenic phases. Some parameters belonging to this category are shown in the following table (Table 3).

Table 3: Range of oscillation of some characteristic parameters of leachate for which no significant trend is observed between the acidic and methanogenic phases.

Parameter	Unit of measurement	Min	Max
Ammonium (NH_4^+)	mg/l	30	3000
Nitrates (NO_3^-)	mg/l	0.1	50
Nitrites (NO_2^-)	mg/l	0	25
Chloride (Cl^-)	mg/l	100	5000

Therefore, during the various stages of leachate production, a clear decrease in organic load and a reduction in the concentration of dissolved "heavy" metals (in leachate) are observed as the biostabilization progresses. This is because as the pH increases from the acidic phase to the methanogenic phase, there is a possibility of their precipitation as hydroxides ($M_x(OH)_y$) or carbonates ($M_x(CO_3)_y$) [M = generic metal; x and y are stoichiometric coefficients].

3.5 Qualitative characteristics of leachate

As already highlighted, the qualitative characteristics of leachate undergo variations over time due to different chemical reactions occurring within the landfill. Therefore, it is difficult to speak in general terms about possible concentrations of leachate elements, and it is necessary to distinguish case by case.

It should be noted that one of the causes of the wide range of variation in values is not only the types of waste deposited in the landfill but also other factors such as age, landfill type, climate, etc.

The pH value generally fluctuates within a range around neutrality, from minimum values (pH = 5-6) corresponding to the acidic range, to maximum values in the alkaline range (pH = 8.9), depending on the age of the landfill.

The organic load, evaluated both as BOD and COD, shows exceptional variability, ranging from values below 1000 mg/l to values exceeding 50000 mg/l. The ratios of COD/TOC and BOD/COD, which indicate the quality of organic compounds present and their biodegradability, are also of considerable interest.

Ammonia and nitrogen also exhibit variability in their values. Ammoniacal nitrogen, characteristic of "old" leachates, is the pollutant towards which significant purification efforts are focused.

Metals are present in the leachate, with some occurring in significant concentrations such as iron, manganese, and zinc, while others are present in smaller quantities like chromium and cadmium.

Among the assessments performed on the leachate, the measurement of AOX (Adsorbable Organic Halides) is also conducted. This parameter represents the sum of absorbed halogenated organic compounds, which are carcinogenic substances.

Municipal solid waste is a natural habitat for numerous microorganisms, including some pathogens. The most prevalent microorganism families in landfills are bacteria. A correlation has been demonstrated between bacterial composition and the age of the landfills. It is important to note that bacterial survival is inhibited by high temperatures and low pH values.

The degradation of organic waste associated with the production of biogas is carried out by anaerobic bacterial flora that naturally develops within the oxygen-depleted waste mass.

In the initial period following waste disposal in the landfill, aerobic degradation predominates over anaerobic degradation due to the presence of trapped oxygen in the waste material. Biodegradation primarily affects carbohydrates, fats, and proteins, which undergo transformations.

These biochemical transformations lead to the production of volatile acids, subsequently converted into methane and carbon dioxide. The degradation of proteinaceous materials also results in the formation of small quantities of undesirable gases such as NH_3, H_2S, and others, which accompany the produced biogas.

The biochemical transformation can be divided into two distinct phases performed by two different bacterial strains:

1. Acid transformation carried out by acid-producing bacteria capable of converting biodegradable materials into volatile acids. This phase leads to a decrease in the waste pH value.
2. Transformation of volatile acids into methane by methanogenic bacteria. This basic transformation slightly increases the pH (7.5-8.2).

Completion of both phases results in the destruction of the volatile solids comprising the waste and its mineralization.

Regarding leachate, the direct consequences on its qualitative characteristics are evident. The most significant variations are as follows:

- The pH tends to increase over time, transitioning from the acidic range in the early stage of the landfill (acidic phase) to the alkaline range (methanogenic phase).
- The content of organic matter expressed in terms of BOD and COD is initially extremely high but subsequently decreases due to biological degradation and leachate percolation.
- The BOD/COD ratio, an indicator of biodegradable organic matter relative to the total, significantly decreases with landfill age due to the decomposition of biodegradable organic matter.
- Ammonium ion concentrations are high due to the hydrolysis and fermentation of proteins from biodegradable organic matter in the initial acetate phase, but theoretically should decrease over time due to substrate depletion in the second (methanogenic) phase.

- Metal content is initially very high in young landfills, as low pH values favour solubilization, but generally tends to decrease over time.
- In anaerobic conditions, sulphates are reduced to sulphides and, therefore, show a decreasing trend, while chlorides decrease due to leaching.

The design characteristics of landfills and their management methods have a significant impact on the quantity of leachate produced. However, it is not easy to determine which parameters influence leachate quality and how they affect the hydrological balance.

One dependency factor is undoubtedly the type of waste deposited in the landfill (which varies over time). Concerning management methods, it is possible to accelerate the decomposition processes of organic matter, as the methanogenic phase is associated with higher-quality leachate. To achieve this, the following measures can be taken:

- Adding buffer solutions or nutrient-rich solutions to the waste.
- Adding sludge from wastewater treatment plants to the waste.
- Adding compost or similar substances to the waste.
- Recirculating leachate within the landfill.

Additionally, there are design considerations that can influence the hydrological balance, including:

– Choosing the material and thickness of the surface cover layer.
– Proper separation of stormwater during landfill cultivation.
– Maintenance of plants and vegetation cover on the final cover soil.
– Methods of landfill bottom and wall sealing.
– Waste compaction level.
– Cultivation time and thickness of the waste layer deposited.

3.5.1 Organic content of landfill leachate

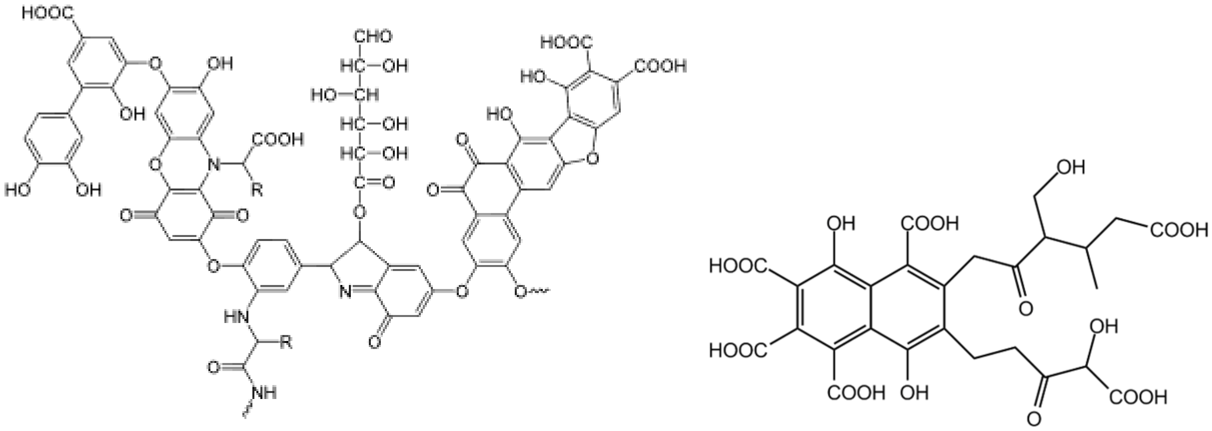


Figure 10. Hypothetical structures of humic and fulvic acids [12]

When all the biodegradable organic matter has been degraded, there is no further production of methane and volatile organic acids. The COD value remains around 100 mg/l of O_2 due to the organic matter that is refractory to biological degradation, mainly composed of humic and fulvic acids. The hypothetical structures of these compounds are shown in Figure 10 , as proposed by Schulten and Schnitzer[27] [28].

These acids are the most abundant fractions of the binding fractions of natural organic matter, in which, as previously mentioned, there can be a high heterogeneity of structure due to the significant variation in the types of binding sites: -COOH and -OH, -NH and -SH, as well as their ratios. In particular, the -SH group can be abundant when formed in anaerobic environments, as can occur in landfill leachate [29] [30] [31].

Therefore, considering the potentially high content of dissolved organic matter (DOM) in landfill leachate, which possesses a large number of functional groups with acid-base properties and complexing capacity towards different metals, it is possible to treat the leachate as an aqueous solution composed of one or a mixture of polyelectrolytes. This assumption allows for the study and treatment of experimental data acquired during the course of this thesis work, using an empirical approach that can help study and determine both the protonation constants of the leachate and its interactions with metal cations [32] [33].

Such data are essential as they can provide information on the hazardous nature of leachate in terms of environmental contamination, as it can become a potential carrier for metals through soils and towards groundwater or surface water bodies.

4 Contaminated sites

Article 242 of Legislative Decree 152/06 establishes the administrative procedures and practices to be implemented in the case of potential contamination from both historical sources and events that may pose risks to the environment.

The text states:

"In the event of an occurrence that has the potential to contaminate the site, the party responsible for the pollution shall implement the necessary preventive measures within twenty- four hours and shall immediately notify the relevant authorities in accordance with Article 304, paragraph 2. The same procedure applies to the identification of historical contaminations that may still pose risks of exacerbating the contamination situation."

In addition to implementing preventive measures to prevent the situation from worsening, the party responsible for the pollution conducts a preliminary investigation in the areas affected by the contamination.

At this point, two possible scenarios arise:

1. The measured values do not exceed the CSC (contamination threshold concentration). In this case, the entity undertakes the restoration of the contaminated area and notifies the competent municipality and province through a self-certification. The site is deemed "non-contaminated."
2. The measured values exceed the CSC for even a single parameter. The site is deemed "potentially contaminated."

In the case of the second point, the responsible party must notify the competent municipality and province, describing the preventive measures and emergency security measures adopted.

The next step is to submit the site characterization plan to the region with territorial jurisdiction within thirty days (which will be discussed in detail in the next paragraph).

Based on the results of the site characterization procedures, the site-specific risk analysis procedure will be applied to determine the RTCs (risk threshold concentrations).

The criteria for the application of the risk analysis procedure are outlined in Annex 1 to Part IV of Legislative Decree 152/2006.

The results of the risk analysis must be submitted to the region within six months of the approval of the characterization plan.

Again, two possible outcomes can occur:

1. The CSC values do not exceed the CSR values. The conference of services must approve the conducted risk analysis, and the process is declared concluded. Site monitoring may be required. Within sixty days of the approval, the responsible party must submit a monitoring plan to the province and region, identifying the parameters to be monitored, as well as the frequency and duration of the monitoring. If the monitoring activities detect the exceedance of one or more risk threshold concentrations, the party must initiate the remediation procedure.
2. The CSC values exceed the CSR values. The party is required to submit the operational project for remediation or operational or permanent security measures within the following six months of the risk analysis approval. The project will be approved by the province and the relevant municipality. The project approval also includes the definition of implementation timelines and any necessary prescriptions for the execution of the works.

The criteria for selecting and implementing remediation and environmental restoration measures, as well as operational or permanent safety measures, involve identifying the best available techniques at sustainable costs (BATNEEC - Best Available Technology Not Entailing Excessive Costs).

In the upcoming chapters of this document, the procedures for properly drafting the site characterization plan and the main remediation procedures for environmental restoration will be further examined.

4.1 Site Characterization Plan

The criteria for the proper preparation of a site characterization plan are outlined in Annex 2, Part IV, Title V of Legislative Decree No. 152 of 2006.

Starting with the definition of a site characterization plan, it can be identified as "the set of activities that allow for the reconstruction of contamination phenomena affecting environmental matrices, in order to obtain basic information on which feasible and sustainable decisions can be made for the security and/or remediation of the site. The characterization activities must be carried out in a manner that allows for the validation of the final results by Public Authorities within a realistic and shared framework of the potentially identified contamination situations."

The development of a site characterization plan must follow a series of phases, which are as follows:

1. Reconstruction of the site's history, with particular attention to the activities carried out.
2. Development of a Preliminary Conceptual Model of the Site (CMS), aimed at preparing the necessary environmental investigations to understand the environmental condition of the natural matrices present (soil, subsurface, and groundwater).
3. Execution of the planned investigations, including any necessary supplementary investigations based on the initial findings.
4. Analysis of the investigation results, in conjunction with the historical data collected in point 1, and representation of the contamination status of soil, subsurface, and groundwater.
5. Development of the Final Conceptual Model.
6. Identification of acceptable residual concentration levels. These levels will be necessary for determining any security measures and/or remediation interventions following the risk analysis conducted according to the criteria outlined in Annex 1, Part IV, Title V of this decree.

The environmental characterization will be initiated following the approval of the Competent Authorities of the Investigation Plan. The conclusion of the plan will occur either at point 5, when the Competent Authorities determine that the entire process does not exceed the CSC, or at the end of all the remediation and/or security measures activities at point 6, in case the CSC are exceeded.

4.2 Preparation of the Environmental Investigation Plan

To write an investigation plan, it is necessary to rely on existing data and establish a preliminary conceptual model. The initial draft of the plan includes the investigations to be conducted, sampling and analysis procedures to be carried out through on-site and laboratory tests. Subsequently, it is supplemented with any additional investigations required to define the environmental condition of the subsurface and acceptable concentration levels for soil and groundwater.

The preliminary conceptual model is developed based on available historical information prior to the start of the investigation plan, as well as any surveys conducted on various environmental matrices during the site's regular management. It includes:

- Specific site characteristics and potential sources of contamination (waste and material storage areas, underground and above-ground tanks, leach pits, etc.)
- Preliminary extension, characteristics, and quality of the environmental matrices affected by the existing or past activities on the site.
- Potential pathways for migration of contamination sources to identified targets

This model needs to be developed before fieldwork begins to provide guidance for defining the Investigation Plan. It is also necessary to define the hydrological situation of surface and deep aquifers based on available historical information, as they can serve as potential carriers of contamination. Tables 4, 5 and 6 list the data and information required for the development of the landfill site's conceptual model.

The investigation plan contains a detailed description of the activities to be carried out in the field and laboratory to characterize the site under examination, along with technical specifications for execution (sampling procedures, field measurements, methods of sample identification, preservation, and transportation, etc.). Once approved by the Competent Authority before the commencement of work, these specifications will form the applicable protocol for site characterization.

The objectives of the investigations are as follows:

- Verify soil, subsurface, and groundwater contamination; determine the degree and volumetric extent of contamination; delimit the volume of waste burial areas.
- Identify possible pathways of pollutant dispersion and migration from sources to potential receptors.
- Reconstruct the geological and hydrogeological characteristics of the area to develop the final conceptual model of the site.
- Obtain the necessary parameters to conduct a detailed site-specific risk analysis.
- Identify potential receptors.

Table 4: List of data and information required for the development of the landfill's CMS.

Survey field	**Necessary data and information**	**Sources of origin according to the type of landfill**		
		Existing controlled landfills	Planned landfills	Existing uncontrolled landfills
Landfill	Geometric characteristics: area, depth, volume, subdivision into lots	Data provided by the operator	Design data	Results from direct and indirect investigations, such as geophysical, geoelectrical, and point surveys
	Types of incoming waste: flows, ((commodity composition))	Data provided by the operator on the waste currently deposited	Waste proposed for authorization and design data for future flows	Results from sampling and analysis of deposited waste
	Operational methods: filling, compaction, daily cover	Information provided by the operator	Information deduced from project documents	Information that is difficult to obtain in the majority of cases
	Characteristics of waste in the landfill: bulk density, hydraulic conductivity, moisture content	Data provided by the operator	Design data for bulk density and literature data for other properties	Results from on-site investigations
	Construction characteristics: lining system for the bottom, side walls, and final surface	Data provided by the operator	Design data	Unavailable information
	Properties of lining systems: thickness, density, hydraulic conductivity	Data provided by the operator	Design data	Unavailable information
	Composition of leachate	Historical data provided by the operator from sampling of extracted leachate	Results from sampling and analysis of existing leachate	Literature data

Table 5: List of data and information required for the development of the landfill's CMS.

Survey field	Necessary data and information	Sources of origin according to the type of landfill		
		Existing controlled landfills	Planned landfills	Existing uncontrolled landfills
Landfill	Biogas composition	Historical data provided by the operator from sampling of collected biogas	Literature data	Results from monitoring surface emissions
	Characteristics of technical systems: leachate collection system, biogas capture system, biogas combustion flares, biogas energy recovery engines	Data provided by the operator	Literature data	Unavailable information
Hydrology	Identification of surface water bodies	Data obtained from site inspections or topographic maps		
	Quantification of surface water flows	Data obtained from site inspections or topographic maps		
	Characterization of surface water quality	Data obtained from site inspections or topographic maps		
	Identification of relationships between groundwater and surface water	Data obtained from site inspections or topographic maps		
Geology and Hydrogeology	Identification and description of geological formations	Data obtained from previous surveys and geological reports		Data obtained from previous geological reports or results from characterization surveys
	Identification and description of existing aquifer systems	Data obtained from previous surveys and geological reports		Data obtained from previous geological reports or results from characterization surveys
	Hydraulic characteristics of the unsaturated zone and underlying aquifer	Data obtained from previous surveys and geological reports		Data obtained from previous geological reports or results from characterization surveys

Table 6: List of data and information required for the development of the landfill's CMS.

Survey field	**Necessary data and information**	**Sources of origin according to the type of landfill**		
		Existing controlled landfills	Planned landfills	Existing uncontrolled landfills
Geology and hydrogeology	Characterization of groundwater quality (including classification of aquifer vulnerability)	Data obtained from local authorities or previous hydrogeological studies		
	Identification of potential receptors: aquifers, water supply wells (with details on water usage)	Data obtained from site inspections, local authorities, or previous hydrogeological studies		
Meteorology	Historical meteorological data: precipitation, winds	Data provided by the landfill operator or local authorities	Data provided by local authorities	
Surrounding site	Soil history and development	Information provided by local authorities		
	Land use	Information provided by local authorities		
	Description of local topographic characteristics	Information provided by local authorities or from site inspections		
	Identification of potential receptors: scattered houses, urban centers, residential areas, industrial zones	Information provided by local authorities or from site inspections		
	Identification of other external sources of contamination, such as agricultural activities, industrial activities, domestic and wastewater treatment plant discharges	Information provided by local authorities or from site inspections		
	Characterization of the impact on water quality caused by other external sources of contamination	Data obtained from local authorities or previous studies		

In order to achieve the above-mentioned objectives, the following must be defined:

- The location and type of investigations to be carried out, both direct (such as boreholes and piezometers) and indirect (such as geophysical surveys).
- The sampling plan for soil, subsoil, waste, and groundwater.
- The plan for physico-chemical analysis and the analytical methods to be used.
- The depth to be reached with drilling, ensuring the protection of deep aquifers and avoiding the risk of contamination induced by sampling.
- The methodologies for interpretation and presentation of results.

4.3 Sampling Point Locations

For each environmental matrix being investigated (soil, subsoil, groundwater), two main strategies can be employed to select the location of sampling and drilling points:

1. Reasoned Location: Based on available historical data and the information synthesized in the preliminary conceptual model, this method aims to verify the hypotheses formulated in the aforementioned model regarding the presence, extent, and potential spread of contamination. This method is chosen for complex sites where historical and plant-related information allows for predicting the location of the most vulnerable areas and the most probable sources of contamination.
2. Systematic Location: The choice of sampling points is made according to a random or statistical criterion. This method is selected when historical information is scarce or incomplete, and it does not allow for obtaining a satisfactory preliminary characterization or predicting the location of the most probable sources of contamination.

Depending on the complexity of the site, both approaches can be simultaneously applied, depending on the different use of areas within the site.

The following methods (shown in Figure 11) for positioning the sampling points are identified:

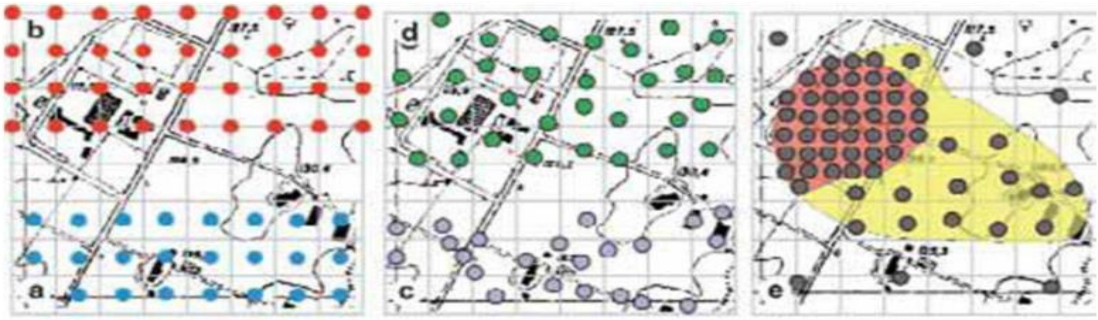


Figure 11: methods for positioning the sampling points

"a" and "b" Systematic or Grid: The sampling points are located at the center or vertices of an ideal grid and are evenly spaced. The sampling density is one sample per grid cell throughout the entire area.

"c" Random: The sampling points are distributed randomly and/or based on site accessibility, and the distance between two points varies.

"d" Systematic-random: In each cell, a randomly positioned sampling point is located. The sampling points are not equidistant, but the sampling density is uniform across the entire investigated area.

"e" Stratified: The area is horizontally and/or vertically divided into sub-areas based on a specific criterion or characteristic (e.g., lithology, permeability, presence of pavement, type of contaminants, operational areas), and the most appropriate sampling point location criterion is applied to each sub-area.

In addition to the aforementioned criteria, the application of indirect investigation techniques, where applicable (e.g., analysis of interstitial soil gas, indirect geophysical surveys, etc.), can be used to determine a better location for direct investigation points and achieve greater areal coverage of information. In this case, the proponent can submit a plan for further investigations, using indirect investigations to formulate the preliminary conceptual model of the site and agreeing with the competent authorities on the methods for discussing and approving the progress of the investigations.

To determine the quality of environmental matrices (background values) in the surrounding environment of the site, it is also necessary to collect samples from adjacent areas. These samples are used to determine the concentration values of pollutants for each relevant environmental component in the site under examination.

4.4 Selection of pollutants to be investigated

The selection of parameters to be investigated is based on the following process:

- Examining the production cycle and/or historical data of the site (industrial process, raw materials, intermediates, products, and waste generated in the case of a discontinued industrial area) to define a "standard set" of analytes that can conceptually be applied, during the investigations, to the majority of the areas of interest. In the specific case of a landfill, it is necessary to consider the disposed materials and the age of the landfill, and all those compounds typically present in the leachate should be searched for.

- Examining the physical state, stability, and actual hazard characteristics of the substances identified in the "standard set" of analytes mentioned in the previous point in order to perform a complete laboratory characterization only on these substances.
- In locations far from potential sources of contamination, a limited number of indicator parameters can be selected based on the toxicity and mobility of the contaminants and their transformation products.

The choice can be simple or extremely complicated depending on the cases. The more detailed the information on the activities conducted on-site and any incidents that may have dispersed chemicals in the environmental matrices, the more it will be possible to narrow down the list of compounds to be investigated, keeping in mind that the cost of chemical analysis almost always represents the most significant expense item in an environmental investigation.

Apart from specific cases where it may be necessary to search for a particular substance, in most cases, the choice must be made for families of compounds (metals, total hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated aliphatic compounds, pesticides, etc.) for which chemical laboratories usually offer an analytical "package".

4.5 Control activities

Control activities carried out by Public Authorities are mainly qualitative and can be performed during field activities by verifying the implementation of the specifications defined in the Investigation Plan. The site manager must ensure the description of field activities through the preparation of a Work Journal, which will be checked and validated by the responsible authorities in charge of the control.

Checks are also carried out in the laboratory during the analyses to verify the correct application of analytical methods, the systems used, and compliance with good laboratory practices. The operational phases in the laboratory, including the control activities by the responsible authorities, will also be described in the laboratory work journal, which can be subjected to verification by the respective authorities.

4.6 Groundwater: matrix characteristics

An aquifer is defined as a formation or group of formations consisting of rock and/or loose soil, whose void spaces within the solid matrix are saturated with water that can move depending on the permeability of the aquifer itself (Figure 12). This water constitutes the water table. The state and quantity of water contained in the soil allow for the distinction of three zones along a vertical profile, from top to bottom:

- Unsaturated zone
- Capillary fringe
- Saturated zone or aquifer.

The unsaturated zone is the portion of the subsurface immediately below the surface where the rock fractures or void spaces between soil particles are not completely filled with water, and this water is capable of moving downwards due to gravity.

The capillary fringe constitutes a transitional zone between the unsaturated zone and the water table. In this zone, the pores are almost entirely filled with liquid, which is retained by capillary action at a pressure increasing with depth but always lower than atmospheric pressure. Its thickness varies considerably with the soil particle size, ranging from a few centimetres in gravel to a couple of meters in clay.

The saturated zone or aquifer contains the groundwater, and its boundary with the capillary fringe is the piezometric surface, defined as the surface along which the pressure of the groundwater is equal to atmospheric pressure. Within the aquifer, all pores or fractures are saturated with water, which predominantly moves horizontally due to a pressure gradient.

The portion of soil affected by fluctuations in the water table, and therefore alternates between saturated and unsaturated conditions, is called the fluctuation zone of the water table (also known as the smear zone).

At the base of the aquifer, there is always an impermeable or low-permeability substrate that supports the water table and prevents or restricts downward flow. An unconfined or free aquifer (in which case the term water table or phreatic surface is preferred) is one in which the piezometric surface coincides with the free surface of the water, known as the phreatic surface, which can freely fluctuate depending on the recharge conditions.

On the other hand, a confined aquifer is one that is also bounded from above by a low-permeability formation, and the piezometric surface is at a higher elevation than the confining formation. In practice, when a piezometer is installed in such an aquifer, the water rises in the piezometer tube to a level above the aquifer roof. This occurs because the water pressure at any point in the water body is greater than atmospheric pressure. If the water pressure is sufficient to cause the water to rise in the piezometer above the ground surface, the confined aquifer is called an artesian aquifer, a term derived from the French region of Artois where this phenomenon was first studied. However, the condition of an artesian aquifer may depend on time, both due to natural adjustments of the medium and the degree of water exploitation to which the aquifer is subjected.

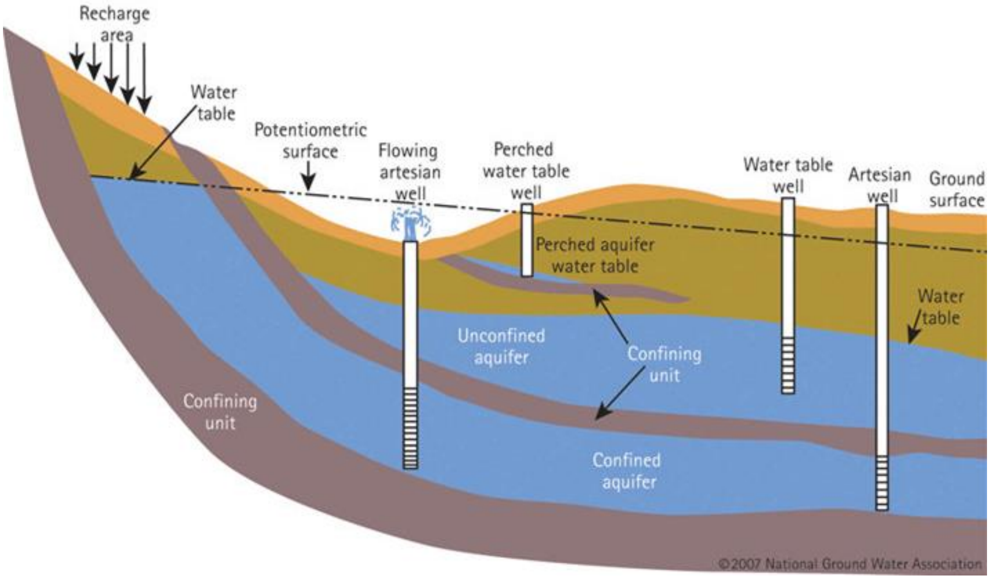


Figure 12: Representation of different types of underground aquifers in relation to the piezometric level.

4.7 Monitoring Piezometers

The term "piezometer," literally meaning "pressure meter," in the field of hydrogeology refers to an observation well used to measure the hydraulic head of an aquifer at a certain depth.

The use of piezometers allows for the reconstruction of the piezometric surface of the aquifer, which is the surface at which the water pressure is equal to atmospheric pressure. In practice, the piezometric surface is reconstructed by interpolating measurements from multiple piezometers in the investigated area. Reconstructing the piezometric surface helps define the hydraulic gradient and flow direction of the groundwater.

Piezometers are also valuable in environmental geology as they enable direct measurements and sampling of groundwater at different depths. Compared to wells, piezometers have smaller diameters and shallower depths, and they are only occasionally equipped with a pump for groundwater extraction.

Depending on whether the installed piezometer or piezometer network serves periodic or occasional groundwater monitoring, they are classified as either permanent or temporary:

- Permanent piezometers are constructed with features that ensure their long-term durability and prevent interference with the chemical and hydrological equilibrium of the aquifer.
- Temporary piezometers are installed for the time necessary to acquire chemical, physical, environmental, and hydrogeological parameters, after which they are sealed or extracted by backfilling the borehole. Therefore, temporary piezometers are typically of very small diameter (<2") and can be quickly installed.

The main components of a piezometer (Figure 13) include:

- Casing (blind pipe)
- Screen (perforated pipe)
- Bottom plug
- Drain
- Seal
- Cementing
- Well box
- Well cap

The choice of materials for completing the well or piezometer is of great importance, as it ensures durability against physico-chemical degradation caused by contaminants. In the presence of chemically reactive aqueous solutions, certain components could be released into the collected samples, rendering them no longer representative. Therefore, the materials used for the tubing should be selected considering potential interactions with the substances present in the aquifer. A resume of advantages and disadvantages for different pipe's material is shown in Table 7.

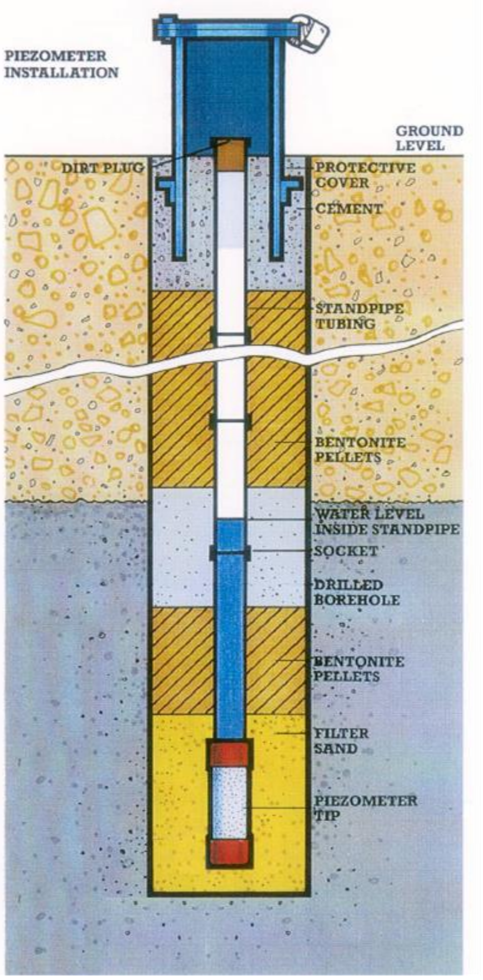


Figure 13: Scheme of a piezometer

Table 7: Comparison of PTFE, Stainless Steel, and PVC Linings: Characteristics

Typology	Advantages	Disadvantages
PTFE (Teflon) pipes	- Can be used over a wide temperature range - Inert to acids and solvents - Easy to construct, install, and extract - Most suitable for monitoring metals	- Can adsorb/desorb organic substances from the solution - Can exhibit ductile behaviour near grooves (e.g., slotted pipes) - The extreme flexibility of PTFE can cause tubing bending and the installation of non-vertical wells - The non-rigidity of PTFE can result in inefficient sealing of the annular space - They have moderate weight and low strength per unit length - They have a relatively higher cost compared to stainless steel and PVC pipes.
Stainless-Steel Pipes	- High resistance over a wide range of - temperatures - Easily accessible - Availability of wide-slotted windows (for slotted pipes) - Suitable for driven wells - Not susceptible to organic substances - Low potential for absorbing organic substances - Most suitable for monitoring organic substances	- Can corrode under specific geochemical and microbiological conditions - Can adsorb cations and anions - Can release metallic ions (iron, chromium, nickel, manganese) into water samples - Have a high weight per unit length - Require on-site welding for joining various components (blind pipe sections, screens, bottom plugs) - Stainless steel 304 and 316 are not suitable for monitoring inorganic substances.
PVC pipes	- Resistant to galvanic and electrochemical corrosion - Modest weight allows for easy installation - High resistance to abrasion - Requires low maintenance - Flexibility and workability for cutting and joining - High strength and low weight per unit length - Easily available - Lower cost compared to PTFE and stainless-steel pipes - Availability of wide-slotted openings (for slotted pipes) - Represents a good choice for monitoring both organic and inorganic substances at low concentrations	- Can degrade in the presence of certain organic solvents, especially low molecular weight ketones, amines, aldehydes, chlorinated alkenes, and alkanes - Can yield under high differential pressures, as they are more brittle and less rigid than steel pipes - Can yield under high temperatures (e.g., during cementation) - Prolonged exposure to certain thermoplastic materials, ultraviolet radiation from sunlight, and/or low temperatures can cause brittleness and gradual loss of impact resistance.

The portion of the piezometer that allows groundwater to enter is called the filter. It consists of a series of small openings (slots) evenly distributed on the surface of the tube, which allows water to pass through while retaining soil particles without weakening the structure of the piezometer.

Although there is a wide range of filters with various shapes and sizes of slots, the most commonly used filters are Johnson filters in combination with steel pipes and PVC filters with pipes made of the same material.

Both types of filters have extremely fine slots on the tube wall, the width of which varies and must be determined based on the aquifer's grain size (Figure 14).

Figure 14: Detail of the slots in the slotted portion of a piezometer.

4.8 Field Surveys

A piezometer allows for the measurement of groundwater depth relative to the ground surface, the measurement of certain physicochemical parameters of groundwater, the collection of water samples, monitoring the operation of a nearby pumping well, and the introduction of tracer substances or reagents into the groundwater. The depth of the water table surface relative to the topographic surface is called the water table elevation. Measuring the water table elevation should be done prior to any other operations to avoid altering the water level in the piezometer, especially before operations such as purging and sampling that require water removal.

To ensure that water table elevation measurements taken at different times in a given piezometer are comparable, they must be referenced to a fixed and unchanging point. As a matter of convenience and established practice, this point is often marked on the wellhead using an indelible marker (paint, marker pen, notch).

Water table elevation is measured using a water level meter. The water level meter is a device consisting of a battery-powered reading probe that is lowered into the piezometer using a millimeter or centimeter-marked cable. The electrical circuit is completed when the probe makes contact with the water surface. A sound, often accompanied by the illumination of an LED, indicates that contact with the water has been made, and the depth can be read.

An advanced version of the water level meter, known as an interface probe (represented in Figure 15), is a similar instrument with the additional capability of detecting the crossing of two distinct interfaces using different sounds (usually continuous and intermittent) and/or specific LED indicators. This allows for the measurement of the depth of a potential floating air/oil interface and the underlying oil/water interface. The difference in depth between the two interfaces represents the thickness of the floating phase.

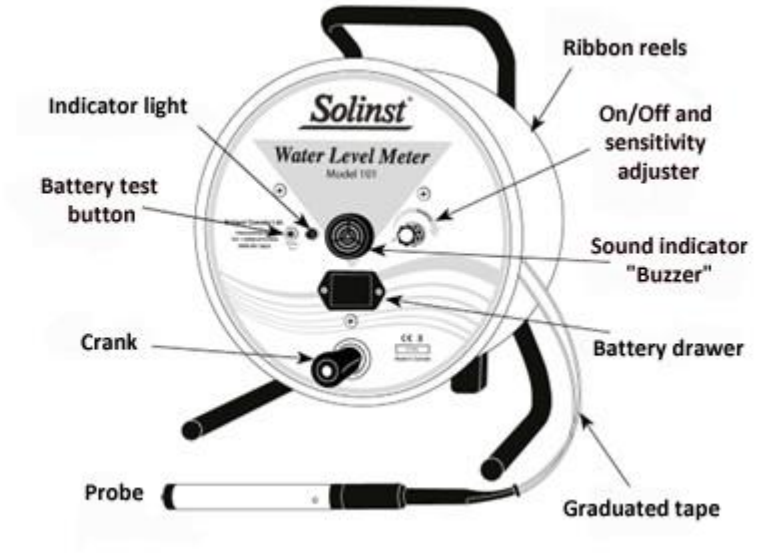


Figure 15: Interface Probe: Enables the measurement of groundwater depth and the thickness of a potential separate liquid phase (NAPL).

4.9 Sampling Techniques

The term sampling refers to a series of field operations. The goal of sampling is to make a representative portion of groundwater available for chemical analysis, representing the physico-chemical state of the aquifer at a given moment. This is possible as long as the sample accurately represents the groundwater system of origin or, at least, a portion of it near the sampling point.

It is essential that the procedures for sampling, preservation, transportation, preparation, and analysis of the sample are suitable for maintaining its representativeness. Before taking a water sample, it is necessary to ensure that it actually represents the groundwater in the vicinity of the piezometer.

Indeed, water may remain trapped inside the piezometer, especially water above the filter section, and may be subject to physico-chemical phenomena that do not affect the aquifer. Additionally, there may be losses of volatile compounds from the water column, mixing with atmospheric oxygen, adsorption of substances on the walls of the piezometer or the well screen, or chemical interactions with bentonite or surface infiltrations. To overcome these issues, every sampling operation must be preceded by proper purging of the piezometer, which involves removing an adequate volume of water and any solid material present.

Purging is typically performed using low-flow pumps (a few liters per minute) that allow water to be removed from the piezometer and its surrounding area without mobilizing soil particles that would render the sample turbid. There are different purging procedures based on different criteria. One criterion is based on the volume of the piezometer. It suggests removing a quantity of water between 3 and 5 times the volume of water present under static conditions inside the piezometer. This is the most commonly followed procedure.

Another criterion involves monitoring certain physico-chemical parameters of the purged water (dissolved oxygen, electrical conductivity, pH, temperature, Eh) until their stabilization is observed. Monitoring can be done using multiparameter probes inserted directly into the piezometer or combined with the use of flow cells.

The term "low flow" refers to the speed at which water enters the pump, specifically the speed imposed on the water present in the soil pores near the filter, rather than the surface flow rate. Applying this method reduces purging volumes, disturbances to the aquifer system, mobilization of soil particles, and stripping of any potentially present contaminants. In particular, reducing the volume of purged water helps address the challenges associated with its disposal, which is often a difficult aspect of the work. After purging, sampling can begin, also using a low-flow approach.

To accomplish purging according to the aforementioned criteria, pumps or bailers can be used. However, some pump manufacturers discourage their use during purging to avoid potential mechanical damage (e.g., wear on impellers and bearings) or electrical issues (e.g., overheating) due to the presence of sediments or foreign bodies in the well water.

Commonly used tools for groundwater sampling include bailers, submerged pumps, suction pumps, and inertial pumps.

Bailers are point samplers consisting of a cylindrical container that is lowered into the piezometer using a cable or rope. They are typically made of stainless steel, HDPE, or PVC for their chemical inertness. Bailers are equipped with a bottom valve consisting of a free-floating sphere inside the sampler. This valve allows water to enter from the bottom during immersion and ensures a seal during the lifting phase. It also facilitates the emptying of the bailer by allowing water to exit from the bottom, reducing excessive aeration, and directing it into the collection container.

Sampling using a bailer does not require prior purging (static sampling), so it preferable to use low-flow pumps to obtain a homogeneous and representative groundwater sample (dynamic sampling) as it minimizes possible alterations to the chemical and physical properties of the water. Static sampling is necessary in cases where groundwater stratification is confirmed or suspected, to check for the presence of a separate phase of immiscible substances, to collect samples in presence of substances with different densities at different depths and/or when the aquifer is no longer productive, as shown in Figure 16.

Figure 16: Bailer just extracted from a well. The liquid exhibits a clear separation between two distinct phases. At the bottom, you can observe groundwater, which appears particularly turbid, with a significant level of opacity. Overlying this aqueous phase there is a layer of floating hydrocarbon product, known as NAPL (Non-Aqueous Phase Liquid).

Centrifugal pumps, one of several types of submersible pumps, consist of a cylindrical steel body, and water is lifted to the surface using a series of impellers (known as rotors) placed inside. These pumps are powered by electronic devices that allow for precise flow control by adjusting the speed of the impellers, enabling low flow rates and so suitable for low-flow samples.

Figure 17: Examples of centrifugal pumps: with steel body (on left) and in plastic (on right).

Centrifugal pumps can be used for piezometers with a diameter greater than 2” and can handle deep water tables (the maximum allowable depth for sampling depends on the pump's head). The main difference from simpler and more economical models lies in the material of the pump body (plastic instead of steel) and the power supply, which operates at 12V, making it possible to power them with a car battery. However, they lack flow rate adjustment. Both types of pumps are suitable for environmental sampling, including volatile compounds, and for short pre-sampling purging. They are not suitable for purging highly turbid water due to their tendency to clog and the delicacy of their internal components. Images of centrifugal pumps are present in Figure 17.

Among submersible pumps, there are also bladder pumps, represented in Figure 18, which are smaller and lighter compared to the previous ones and can be used in small-diameter piezometers (1"). The name comes from the presence of a bladder, which, through a series of compression-decompression cycles generated by a flow of compressed air or gas, allows for water aspiration. Flow rate can be adjusted by changing the pressure of the compressed air (or gas). Another advantage is that there is no degassing of the sample since it does not come into contact with the air.

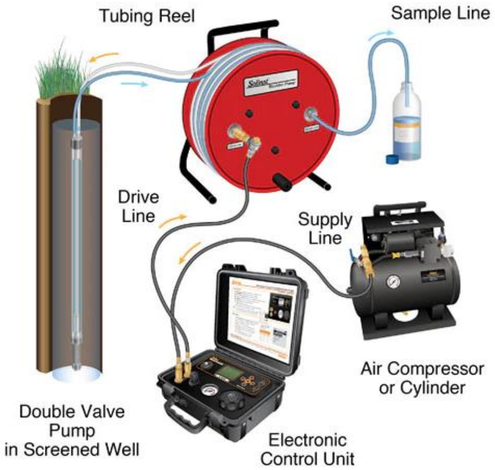


Figure 18: A bladder pump kit.

About suction pumps, there are peristaltic pumps (Figure 20) that consist of a rubber tubing that is lowered into the piezometer and connected to a rotor composed of cylinders which, when rotating, compress the tubing itself, creating a negative pressure capable of drawing water from the piezometer (Figure 19).

Systems like the one described are referred to as "vacuum" systems and have a physical operating limit that is theoretically close to ten meters of water column but in practice is rarely higher than eight. The power supply for these pumps can be manual, for more economical models, or electrically powered (by battery or through the electrical grid). In the latter case, it is possible to adjust the rotational speed and, consequently, the flow rate.

They can also be used in small-diameter piezometers (2"), but it is not recommended for sampling volatile compounds because the pressure difference can cause the extraction of these compounds from the water.

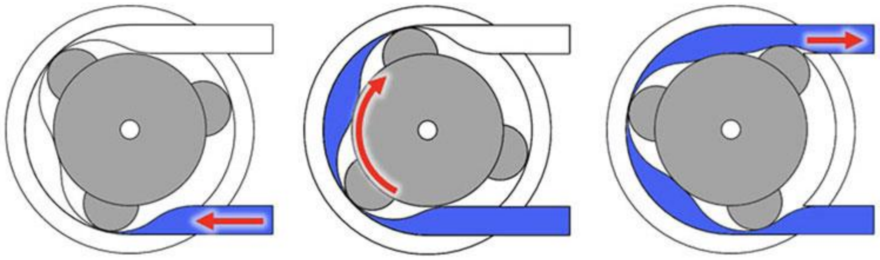


Figure 19: Mechanism inside peristaltic pump

Figure 20: A peristaltic pump

Finally, there are inertia pumps, consisting of a high or low-density polyethylene (HDPE or LDPE) tubing with a non-return valve at the end (Figure 21). The operation is manual and involves alternating upward and downward movements. However, the pumping action does not allow an undisturbed sample, and the water tends to become turbid. To achieve a higher flow rate, you can replace the manual operation with an electric one. It is, however, a very cost-effective sampling method.

In general, the choice of pumps should be based on the groundwater depth, piezometer diameter, the type of contamination present in the groundwater (if known) and the type of compounds being sought.

Figure 21: Inertia pump

The following table highlights the advantages and disadvantages of the most commonly used pump types in the field of environmental geology:

Table 8: Advantages and disadvantages of different types of pumps for environmental monitoring

Type of pump	Advantages	Disadvantages
Submersible pumps powered by the electrical grid	Robustness and resistance to chemical attacks. Adjustable flow rate (on some models, by directly adjusting the impeller rotation speed). High head and flow rate.	High cost. Requires decontamination after each use. Movement of the impeller causes water agitation in the piezometer.
Submersible pumps powered by batteries	Low cost, easy to use even where there is no electrical grid. Pump body modularity to increase head.	Pump body and impellers made of ABS are not suitable for certain contaminants. Requires decontamination after each use. Movement of the impeller causes water agitation in the piezometer.
Diaphragm pumps	Allow for extremely low operating flow rate (<0.5 l/min) with minimal disturbance to the water in the piezometer. High head. Advanced models allow for the replacement of the internal diaphragm after each sampling. No need for electrical power. Suitable for VOC sampling.	The purchase price of the gas cylinder-control unit-pump system is generally higher than in other systems.
Suction pumps	Ideal for low-flow sampling and in-line filtration. The sample never comes into contact with mechanical parts. Suitable for small-diameter piezometers (< 2"). Disposable Teflon tubing.	Maximum head < 10m. Potential loss of volatile compounds.
Inertial pumps	Low cost and easy to use, manually or motorized. Can be used in micro-piezometers (diameter <2"). Disposable tubing.	Operation tends to agitate the water in the well.

The number of samples to be collected in each investigation campaign should be determined on a case-by-case basis based on the project requirements and the availability of a monitoring network.

4.10 Groundwater Sampling Methods from Piezometers

For the various operational phases of groundwater sampling, reference should be made to Annex 2, Part IV, Title V "Groundwater" of Legislative Decree 152/2006, which provides for dynamic sampling and the Guidelines for Groundwater Sampling (ARPACAL - Regional Agency for Environmental Protection of Calabria) [34] , specifically:

a.1 Use low flow rates during purging and subsequent sampling, in dynamic mode using a submersible pump, to minimize the drawdown of the piezometer water level and reduce turbulence.

a.2 Minimize disturbances to the stagnant water column above the fractured interval during water level measurements and insertion of the sampling device (pump).

a.3 Adjust the flow to stabilize the rate as quickly as possible.

a.4 During purging, regularly monitor the characteristic parameters of the aquifer (pH, temperature, conductivity, etc.) until values stabilize (Temperature ± 0.2 °C; pH ± 0.1 pH units; Conductivity ± 3%), as reported in the Operational Procedures Guidelines - Groundwater Sampling (ARPACAL - Regional Agency for Environmental Protection of Calabria) [13].

a.5 Operationally, a flow rate (Q) < 0.5 l/min was used for the application of the method.

a.6 Before all sampling and purging phases of the piezometer, measure the groundwater depth from the wellhead using a water level meter.

7 Collect sample aliquots in appropriate containers (see Table 3) based on the analytes to be analysed and label each container clearly for identification and cross-referencing with the sampling report. Include on each label the well/piezometer name and identification, sampling site, and sampling date.

8 Seal (with cable ties or adhesive tape) and mark each container containing sample aliquots by the personnel participating in the sampling.

9 Transport the samples in suitable containers (portable refrigerators and ice packs) to the laboratory, where they are received and properly stored by designated personnel until they are opened and analysed.

10 Take all necessary precautions during the sampling phases to minimize potential alterations, considering the parameters to be determined, and avoid any form of cross-contamination.

11 Prepare a sampling report following the procedures already mentioned for soil sampling.

4.11 Types of Containers to be Used for Sampling

Table 9 below lists the different types of containers to be used during sampling, transportation, and preservation of samples, based on the type of chemical, physico-chemical, or biological parameter to be determined, as stated in the document "Guidelines-SNPA 13, 2018" of the National System for Environmental Protection[35]: "Sampling of inland waters aimed at determining chemical parameters and field measurement of basic physico-chemical parameters for the Water Framework Directive" (resolution of the SNPA Council. Meeting on 22.02.2018. Doc. No. 25/18).

Table 9: Type of containers to be used based on the parameters to be tested.

Parameters	Types of containers
CHEMICAL-PHYSICAL PARAMETERS (one, all, or some of them), excluding metals, hydrocarbons, volatile organic compounds, IPA, PCB	Polyethylene (PE) containers with airtight cap, filled completely.
METALS	PE containers with airtight cap
Non-metallic inorganic constituents (e.g., nitrates, nitrites, ammonia, chlorides, sulfates, etc.)	PE or glass containers
Fluorides	PE and Teflon containers
COD, BOD$_5$	Glass containers
Volatile organic compounds, including aromatic organic compounds	Glass vials with screw caps, filled completely.
Hydrocarbons, IPA, PCB	Dark glass containers with airtight seals, filled completely.

4.12 Details on the type of analysis to be performed on the water/liquids

The following table (Table 10) presents the analytes to be tested in water and leachate samples. The limit values indicated refer to Table 2 (Groundwater) of Annex 5 to Part IV, Title V of Legislative Decree 152/2006 .

Table 10: analytes to be tested in water and leachate samples

Group	Analyte	Limit values (µg/l)	U.M.
Macro-descriptors*	pH		*u.* pH
	Conductivity at 20 °C		µSiemens/cm
	COD		mg/l
	BOD$_5$		mg/l
	Ammonium		mg/l
	Nitrite	500	µg/l
	Nitrate		mg/l
	Chloride		mg/l
	Bromide		mg/l
	Phosphate		mg/l
	Sodium		mg/l
	potassium		mg/l
	Magnesium		mg/l
	Calcium		mg/l
	Barium		mg/l
Metals*	Aluminum	200	µg/l
	Antimony	5	µg/l
	Silver	10	µg/l
	Arsenic	10	µg/l
	Beryllium	4	µg/l

	Cadmium	5	µg/l
	Cobalt	50	µg/l
	Total chromium	50	µg/l
	Iron	200	µg/l
	Mercury	1	µg/l
	Nickel	20	µg/l
	Lead	10	µg/l
	Copper	1000	µg/l
	Selenium	10	µg/l
	Manganese	50	µg/l
	Thallium	2	µg/l
	Zinc	3000	µg/l
Inorganic pollutants	Boron	1000	µg/l
	Fluorides	1500	µg/l
	Sulfates	250	µg/l
Aromatic organic compounds	Benzene	1	µg/l
	Ethylbenzene	50	µg/l
	Styrene	25	µg/l
	Toluene	15	µg/l
	m+p-Xilene	10	µg/l
	o-xilene		µg/l
Polycyclic aromatic hydrocarbons**	Benzo(a)anthracene	0.1	µg/l
	Benzo(a)pyrene	0.01	µg/l
	Benzo(b)fluoranthene	0.1	µg/l
	Benzo(k)fluoranthene	0.05	µg/l
	Benzo(g, h, i)perylene	0.01	µg/l
	Chrysene	5	µg/l
	Dibenzo(a,b)anthracene	0.01	µg/l
	Indeno(1,2,3-cd)pyrene	0.1	µg/l
	Pyrene	50	µg/l
	Sum (31,32,33,36)	0.1	µg/l
Carcinogenic chlorinated aliphatics	Chloromethane	1.5	µg/l
	Trichloromethane	0.15	µg/l
	Vinyl chloride	0.5	µg/l
	1,2-Dichloroethane	3	µg/l
	1,1-Dichloroethylene	0.05	µg/l
	Trichloroethylene	1.5	µg/l
	Tetrachloroethylene	1.1	µg/l
	Hexachlorobutadiene	0.15	µg/l
	Sum of organohalogens	10	µg/l
Non-carcinogenic chlorinated aliphatics	1,1-Dichloroethane	810	µg/l
	1,2-Dichloroethylene	60	µg/l
	1,2-Dichloropropane	0.15	µg/l
	1,1,2-Trichloroethane	0.2	µg/l

	1,2,3-Trichloropropane	0.001	µg/l
	1,1,2,2-Tetrachloroethane	0.05	µg/l
Carcinogenic halogenated aliphatics	Tribromomethane	0.3	µg/l
	1,2-Dibromoethane	0.001	µg/l
	Dibromochloromethane	0.13	µg/l
	Bromodichloromethane	0.17	µg/l
Chlorobenzenes	Monochlorobenzene	40	µg/l
	1,2-Dichlorobenzene	270	µg/l
	1,4-Dichlorobenzene	0.5	µg/l
	1,2,4-Trichlorobenzene	190	µg/l
	1,2,4,5-Tetrachlorobenzene	1.8	µg/l
	Pentachlorobenzene	5	µg/l
	Hexachlorobenzene	0.01	µg/l
Dioxins and furans	Sum of PCDDs, PCDFs (expressed as TEF)	$4 * 10^{-6}$	g I-TEF/l
Other substances Polychlorinated biphenyls***		0.01	µg/l
Total hydrocarbons (expressed as n-hexane)		350	µg/l

*In addition to the metals and inorganic pollutants listed in lines 1-23 of Table 2 of Annex 5 to Part Four, Title Five of Legislative Decree 152/2006, additional metals, alkaline and alkaline-earth cations, and inorganic anions have been determined.

** In addition to the volatile organic compounds (IPA) listed in lines 29-37 of Table 2 of Annex 5 to Part Four, Title Five of Legislative Decree 152/2006, additional analytes belonging to the same compound family have been determined.

*** The 29 congeners indicated in Annex 3 (sampling and analysis of waste) of Ministerial Decree September 27, 2010 (Definition of criteria for landfill waste acceptability, replacing those contained in the decree of the Minister of the Environment and Territory Protection on August 3, 2005) have been determined[36].

4.13 Contamination indicators (markers) and leachate characterization

Since landfill leachate does not have a standard composition, its chemical and physicochemical characterization allows the identification of potential indicator parameters - "markers" - for the contamination of soil, groundwater, and surface water in the vicinity of a landfill [37] [38] [39] [40] [41].

These markers can be metals or organic species present in natural environments and enable the detection of contamination situations attributable to anthropogenic activities. The assessment of the potential impact resulting from the loss of leachate into soil/subsoil and aquifers can be approximated by comparing the concentrations of different chemical and physicochemical parameters in the leachate with those in groundwater, surface water, or soils sampled in areas outside the landfill site, unaffected by evident anthropogenic activities.

This provides indications of the qualitative and quantitative state of the analyzed matrices under natural and undisturbed conditions, allowing the values of the chemical and physicochemical parameters of such waters to be considered as reference "background" values.

The concentration gradients of a given analyte, measured in a sample not subject to anthropogenic activities, compared to its concentration in a potentially contaminated matrix, can provide precise indications of the potential contamination of the sample itself.

5 Remediation and Security Measures

Remediation of a contaminated site refers to the elimination of pollution from environmental matrices or the reduction of pollutant concentrations in soil, subsoil, groundwater, and surface water to bring them within the values of contamination threshold concentrations (CSC) established for the intended land use or the values of risk threshold concentration (CSR) defined by the specific site risk analysis (Annex 1 Part IV D. Lgs. 152/06[14]).

Security measures, on the other hand, involve the removal and isolation of pollution sources aimed at containing the spread of pollutants to prevent contact with humans and surrounding environmental receptors. There are three types of security measures:

1. Emergency security measures: Immediate or short-term interventions implemented under emergency conditions in the event of sudden contamination events of any nature. These measures aim to contain the spread of primary sources of contamination, prevent their contact with other matrices present on the site, and remove them while waiting for possible further remediation or operational/permanent security measures.
2. Operational security measures: The set of interventions carried out at a site with ongoing activities to ensure an adequate level of safety for people and the environment, pending further permanent security measures or remediation to be implemented upon cessation of activities.
3. Permanent security measures: The set of interventions aimed at permanently isolating the pollution sources from the surrounding environmental matrices and ensuring a high and definitive level of safety for people and the environment.

The security measures for a contaminated site also include monitoring and control actions to verify over time whether the adopted solutions are effective in maintaining pollutant concentration values in the affected environmental matrices below the CSR.

The general criteria for conducting remediation and security measures are as follows:

a) Prioritize remediation techniques that permanently and significantly reduce the concentration of pollutants in different environmental matrices, their toxic effects, and mobility.
b) Prioritize remediation techniques that aim to treat and reuse soil on-site, in-situ and on-site treatment of contaminated soil, thereby reducing the risks associated with the transportation and disposal of contaminated soil.
c) Prioritize permanent remediation/security techniques that immobilize pollutants in stable chemical compounds (e.g., stable crystalline phases for heavy metals).
d) Prioritize remediation techniques that allow for the treatment and on-site reuse of heterogeneous materials or residues used as fill materials.
e) Consider the reuse of soil and heterogeneous materials subjected to off-site treatments, both on the same site and in other sites with suitable environmental and health characteristics.
f) Give preference to the use of high-quality organic materials from urban waste recovery activities in remediation and environmental restoration interventions.
g) Avoid any additional risks of air, groundwater, surface water, soil, and subsoil pollution, as well as any inconvenience caused by noise and odors.
h) Avoid hygienic and health risks for the population during the implementation of interventions.
i) Adjust environmental restoration interventions to the intended land use and the morphological, vegetational, and landscape characteristics of the area.
j) For security measures, prioritize interventions that allow for in-situ treatment and industrial reuse of soils, waste materials, and extracted groundwater, in order to reduce the volume and hazardousness of waste generated.
k) Adapt security measures to the specific characteristics of the site and the environment influenced by it.
l) Avoid any possible deterioration of the environment and landscape resulting from the construction works.

6 Bortolotto large area: general site overview

The large area “Bortolotto” is in the northeastern zone of the municipality of Castel Volturno (CE) (Figure 22).

Figure 22: Display at different scales of the intervention area. The yellow line represents the boundary of the municipality of Castel Volturno, and the red line represents the "Bortolotto" large area.

The intervention area is entirely flat, with a slightly undulating topography due to the presence of areas of fluvial sediment accumulation alternating with slightly depressed areas. There is a dense network of canals designed to drain the reclamation waters towards the sea, as the area was previously occupied by swamps and marshes.

Geometrically, the site has a trapezoidal shape, and the relief of the two landfills within the large area is well defined:

- The oldest and largest landfill is the "So.Ge.Ri" landfill located to the north (covering an area of approximately 12 hectares).
- The second landfill is the "Bortolotto" landfill (covering an area of 4.5 hectares).

Additionally, approximately 110,000 square meters of land, mainly used for agricultural purposes, have been added to complete the area (Figure 22).

The area of interest is within the "Litorale Domitio Flegreo ed Agro Aversano" site but is no longer classified as a site of national reclamation interest according to the Ministerial Decree No. 7 of January 11, 2013, titled "Reclamation Sites that do not meet the requirements of Legislative Decree 152/2006," published in the Official Gazette No. 60 on March 12, 2013 [42].

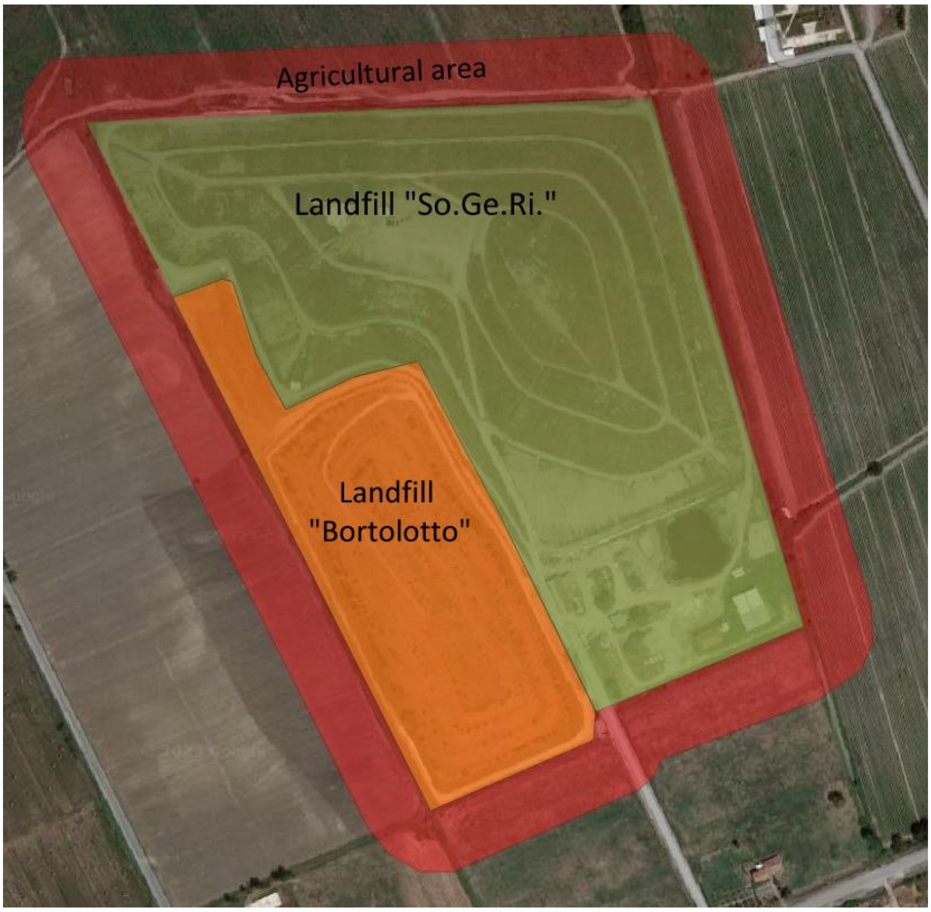


Figure 23: Map of the "Bortolotto" large area showing the subdivision into the three component areas: the "So.Ge.Ri" landfill in green, the "Bortolotto" landfill in orange, and the agricultural land area in red.

6.1 Cartographic framework

For the cartographic framework considerations that will be presented below, reference was made to the Geoportal of the Campania Region - Territorial Information System of the Campania Region (https://sit2.regione.campania.it/content/download).

The area in question falls within the Regional Digital Technical Map of the Campania Region, Elements No. 429 121 (Bortolotto area) and 429 122 (Experimental Agricultural Center), at a scale of 1:5,000, as shown in the following excerpt (Figure 24):

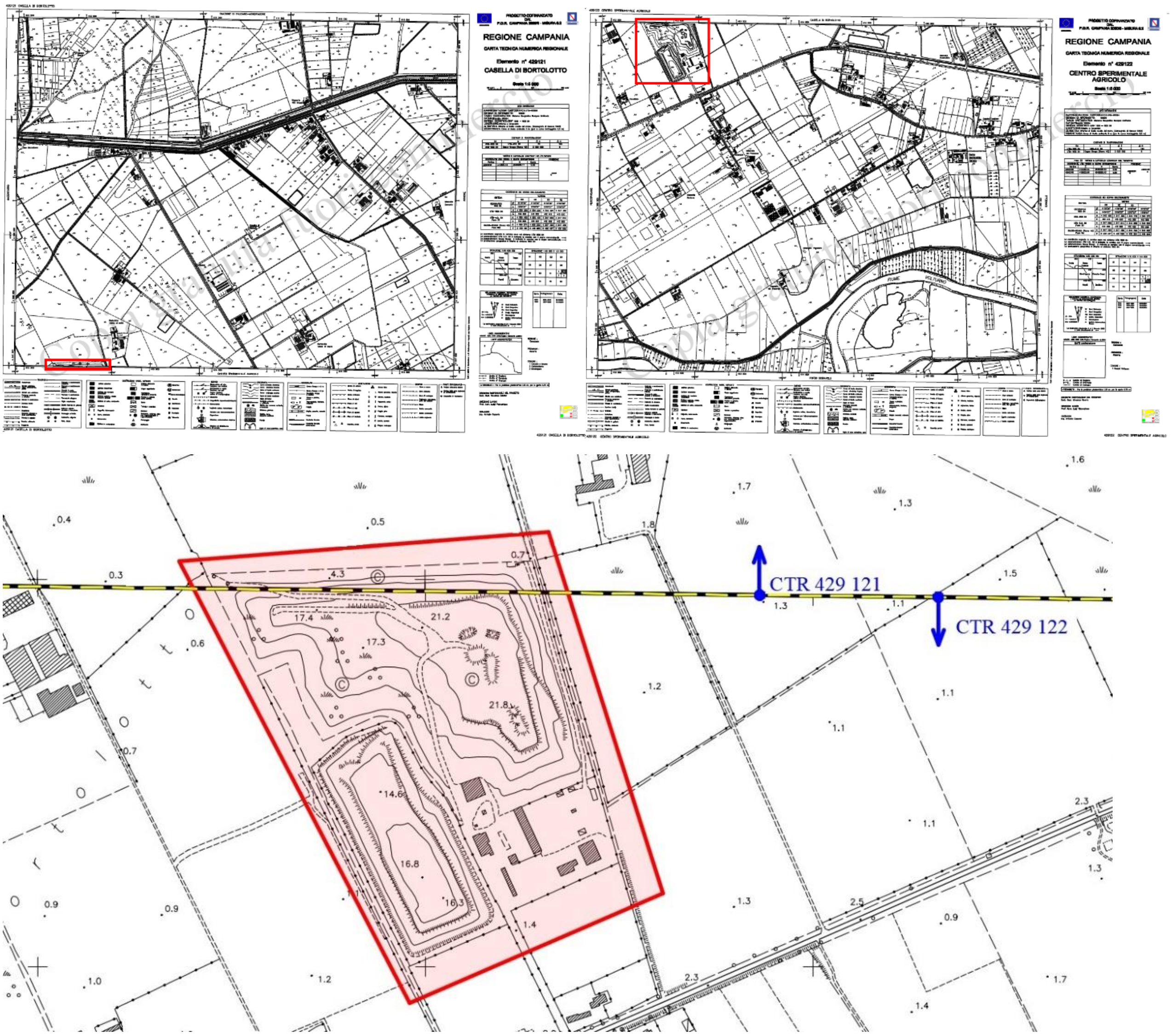


Figure 24: Location of the Bortolotto large area (lower excerpt; shaded in red) represented in the CTR section 429 121 (top left) and the CTR section 429 122 (top right).

From a **cadastral point of view**, the areas under investigation are located in the Land Registry Sheet number 5 of the Municipality of Castelvolturno. The specific parcels are as follows: 86 (Bortolotto landfill), 46, 5005, 63, 76, 91, 90, 5042, 5006, 47, 85, 5036, 5033, 5054, 5070, 5069, 5068 (surrounding agricultural lands). The parcels owned by So.Ge.Ri. S.r.l. are excluded from the characterization (Figure 25).

Figure 25: Cadastral excerpt showing the delineation of the areas under investigation.

6.2 Constraints analysis

For the considerations regarding the constraints analysis of the area, reference was made to the Geoportal of the Campania Region - Territorial Information System of the Campania Region (https://sit2.regione.campania.it/content/servizi-wms) and the tables attached to the PTCP Caserta (adopted under the provisions of Article 20, paragraph 7, Regional Law No. 16/04 [43], with Provincial Council Resolutions No. 15 of 27/02/2012 and No. 45 of 20/04/2012, and approved under the provisions of Article 20, paragraph 7, Regional Law No. 16/04, with Provincial Council Resolution No. 26 of 26/04/2012).

6.2.1 Environmental constraints

In the intervention area, there are no protected natural areas or Natura 2000 network sites as shown in Figure 26.

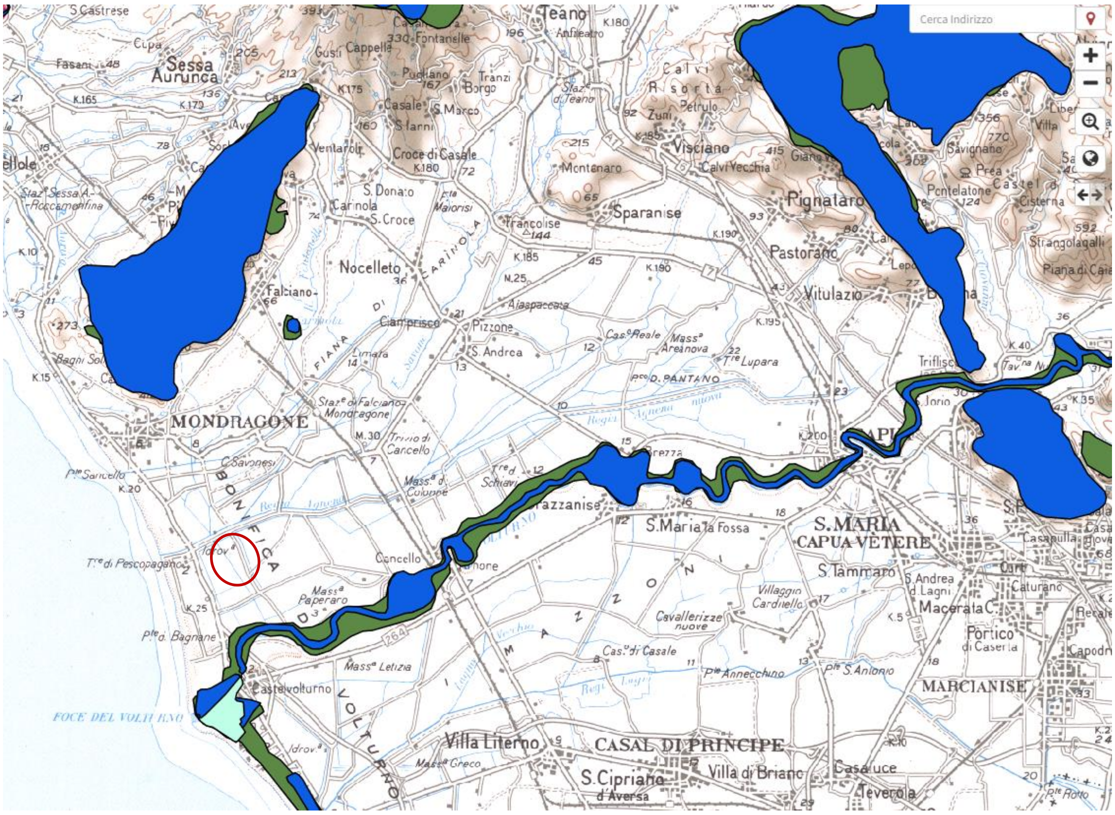


Figure 26: Excerpt from environmental constraints paper (Source: http://www.provincia.caserta.it/ptc/)

6.2.2 Landscaping constraints

From consulting the "Table B3.2.7, Cultural Identity - Landscape Assets" attached to the Caserta Provincial Territorial Coordination Plan (adopted in accordance with Article 20, paragraph 7, Regional Law No. 16/04 [43], with Provincial Government Resolutions No. 15 of 27/02/2012 and No. 45 of 20/04/2012, and approved in accordance with Article 20, paragraph 7, Regional Law No. 16/04, with Provincial Council Resolution No. 26 of 26/04/2012), the intervention site falls within the "coastal strip subject to protection up to a depth of 5000 meters from the shoreline".

No protected areas are identified under Legislative Decree No. 42/2004, Article 142 and 136, in the study area.

Therefore, the project area does not fall within any legally protected areas or properties of significant public interest, as also indicated in the Environmental Report attached to the Regional Plan for the Reclamation of Polluted Sites in the Campania Region (PRB), adopted by D.G.R. 387/2012 (Figure 27).

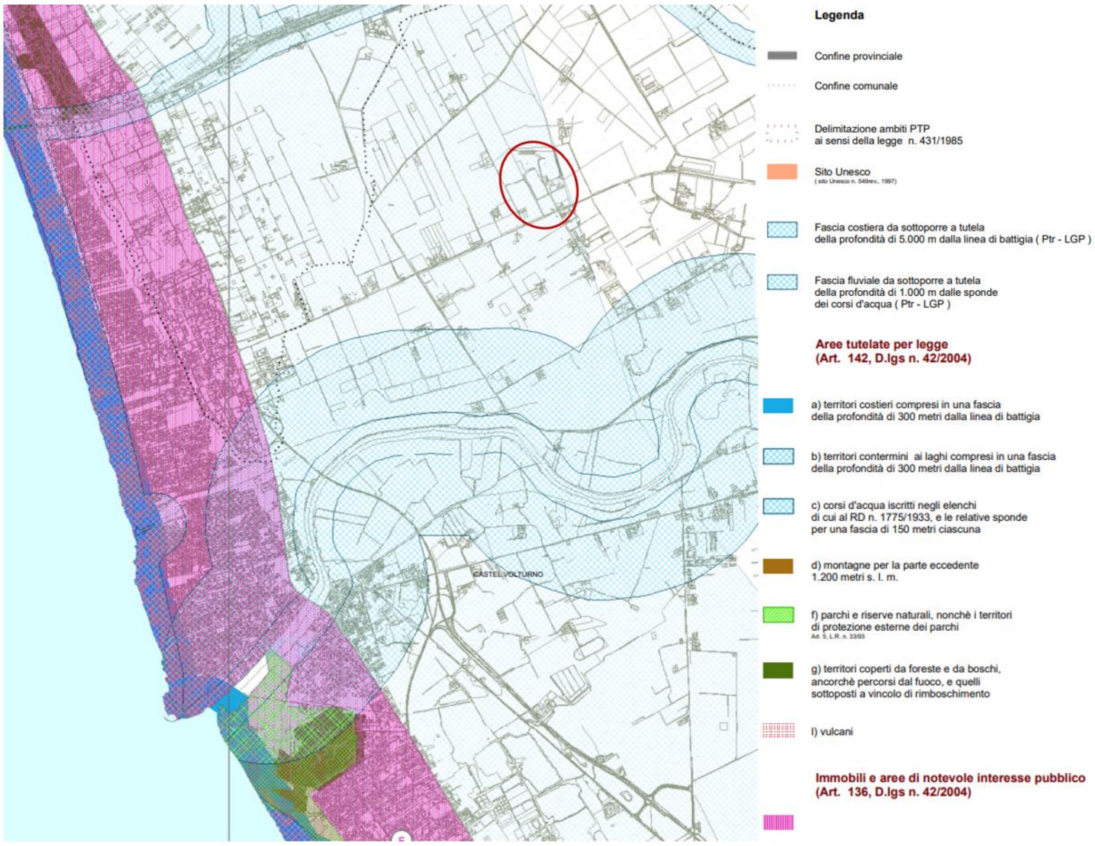


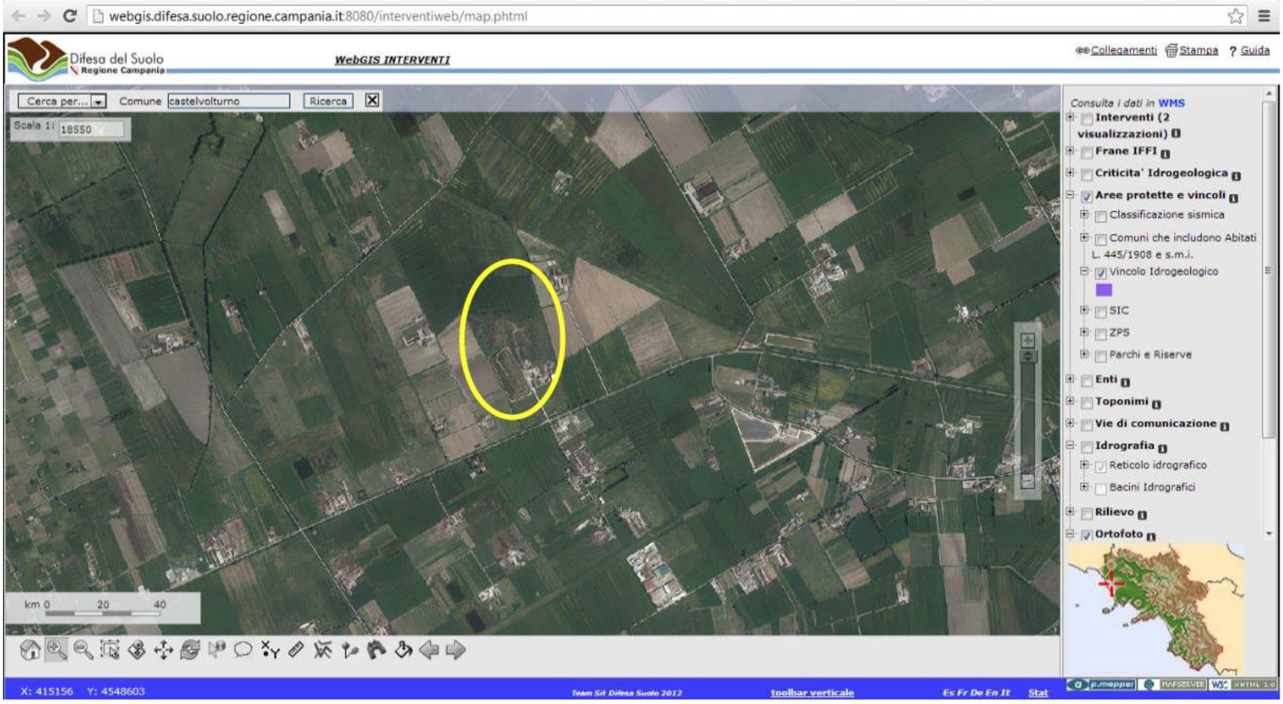
Figure 27: Excerpt from landscape constraints map (Source: http://www.provincia.caserta.it/ptc/)

6.2.3 Archaeological Constraints

From consulting the "Table B3.3.2, Cultural Identity - Archaeological Sites" attached to the Caserta Provincial Territorial Coordination Plan (adopted in accordance with Article 20, paragraph 7, Regional Law No. 16/04 [43], with Provincial Government Resolutions No. 15 of 27/02/2012 and No. 45 of 20/04/2012, and approved in accordance with Article 20, paragraph 7, Regional Law No. 16/04, with Provincial Council Resolution No. 26 of 26/04/2012), the intervention site falls within a "white area," meaning it is not subject to specific requirements or considerations for the proposed activities.

6.2.4 Hydrogeological Constraints

The Hydrogeological Constraint was established and regulated by Royal Decree No. 3267 of December 30, 1923 [44], and Royal Decree No. 1126 of May 16, 1926 [45]. The main purpose of the Hydrogeological Constraint is to preserve the physical environment. It does not prevent the possibility of transforming or newly utilizing the land but aims to protect public interests and prevent public harm. The intervention area of the project does not fall within the areas bound by the "Hydrogeological Constraint, as per R.D. 3267/23," as shown in the following figure extracted from the WebGIS of the Department of Soil Defense of the Campania Region.



webgis.difesa.suolo.regione.campania.it:8080/interventiweb/map.phtml

Comune castelvolturno

Scala 1: 18550

Consulta i dati in WMS
- ☐ Interventi (2 visualizzazioni)
- ☐ Frane IFFI
- ☐ Criticita' Idrogeologica
- ☑ Aree protette e vincoli
  - ☐ Classificazione sismica
  - ☐ Comuni che includono Abitati L. 445/1908 e s.m.i.
  - ☑ Vincolo Idrogeologico
  - ☐ SIC
  - ☐ ZPS
  - ☐ Parchi e Riserve
- ☐ Enti
- ☐ Toponimi
- ☐ Vie di comunicazione
- ☐ Idrografia
  - ☑ Reticolo idrografico
  - ☐ Bacini Idrografici
- ☐ Rilievo
- ☑ Ortofoto

X: 415156 Y: 4548603

Figure 28: Excerpt from hydrogeological constraint map

6.3 Geological stratigraphic, hydrogeological and geotechnical context

The area where the Bortolotto large area is located is part of the extensive plain known as the "Piana Campana," which represents the structural element situated between the Tyrrhenian Sea and the Neogene Apennine Mountain chain. The Piana Campana, along with the Campi Flegrei and Naples areas, represents a tectono-sedimentary structure consisting of large Pleistocene "graben" filled with sediments, from bottom to top, in marine, volcanic-effusive, alluvial, and/or marsh facies. Once these structural depressions were filled and sealed, they formed a low plain that descends in altitude towards the coastline, exhibiting a sub-flat morphology characterized by stable, uniform, and homogeneous profiles with average elevations of 2 meters above sea level.

The most recent and superficial sediments, originating from alluvial and/or marsh environments, are drained through reclamation channels that intersect to convey rainwater towards important surface water bodies such as the Volturno River and the Regi Lagni. With these morphological conditions, the areas are stable, with no significant active geomorphic phenomena.

The hydrogeological structure of the Piana Campana (Figure 29) exhibits aspects of particular complexity due to the significant differentiation in lithological types based on granulometry and degree of fracturing, including various types of rocky formations.

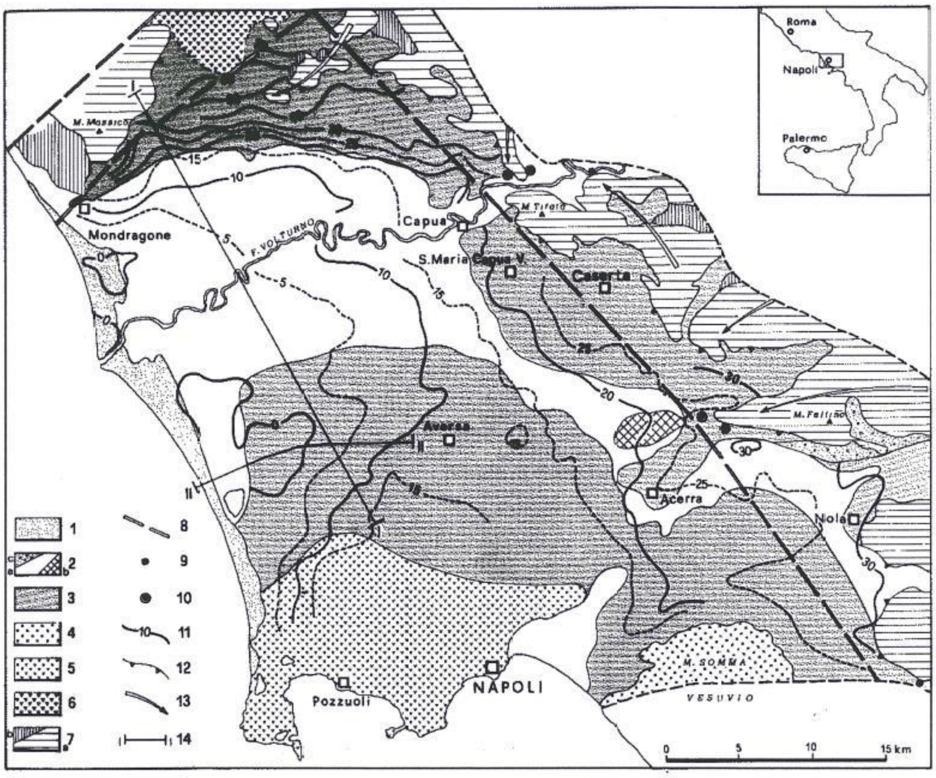


Fig. 1 - SCHEMA IDROGEOLOGICO DELLA PIANA CAMPANA. 1) Depositi sabbiosi e limo-sabbiosi dunari e di spiaggia. 2) Depositi limoso-sabbioso-torbosi fluvio-palustri (a); banchi di travertino (b); detrito di falda (c). 3) Tufi litoidi talora sovrastati da spessori di piroclastiti sciolte. 4) Colate laviche sepolte da potenti spessori piroclastici. 5) Unità tufacee dei Campi Flegrei con a tetto materiali pozzolanici s.l. 6) Prodotti lavici e piroclastici del Roccamonfina. 7) Calcari e calcari dolomitici mesozoici (a); terreni argilloso-arenacei miocenici (b). 8) Discontinuità tettoniche regionali. 9) Sorgenti (Q > 100 l/s). 10) Sorgenti minerali. 11) Isopiezometriche (marzo/aprile 1988) e quote in m s.l.m. 12) Travasi sotterranei dai massicci carbonatici. 13) Direzione e verso di flusso delle falde di base. 14) Tracce di sezione.

Figure 29: Hydrogeological scheme

These litho-structural assumptions decisively influence the permeability, flow dynamics, as well as the quality and quantity of groundwater resources. In general, the depositional sequence can be divided into two main hydrogeological complexes: an alluvial-type surface complex and a pyroclastic complex.

In the area of immediate interest, based on an analysis of bibliographic data and site-specific investigations carried out both in the past and more recently, the lithostratigraphic sequence has been reconstructed, characterizing it from hydrogeological, lithotechnical, and seismic perspectives and represented in Figure 30. Specifically, investigations conducted by the Inter-Municipal Consortium CE/4 in 2002 and the execution of four geotechnical boreholes reaching a depth of -20 meters below ground level in 2012-2013 have provided valuable insights.

The local stratigraphy is characterized by sandy sediments, silty clay with intercalations of peat and silty sands, resting, downward, on pyroclastic soils. Fine-grained sediments are encountered and starting from a depth of 4.0-5.0 meters below ground level, the lithologies vary in grain size from silty clay to silty clay.

Consequently, the geometric-stratigraphic arrangement of subsurface sedimentary bodies in the large area is lenticular, consisting of heterogeneous materials with varying permeability.

The "typical stratigraphic sequence" that characterizes the subsurface of the landfill area is characterized, from top to bottom, by the following lithostratigraphic formations:

a) Topsoil and fill soils (variable thickness ranging from 0.50 to 1.50 meters)
b) Grey silty clay with peaty intercalations (variable thickness ranging from 5.00 to 7.00 meters)
c) Sandy silt (variable thickness ranging from 0.50 to 1.50 meters)
d) Alternation of plastic clays, silts, and peats with gastropod and bivalve remains (variable thickness ranging from 5.00 to 8.50 meters)
e) Pyroclastic-origin sands
f) Grey-yellowish medium-fine-grained sands ranging from silty to weakly silty

In summary, the area is characterized by a thick layer of predominantly clayey and silty materials, generated by the alluvial and deposition phases of the Volturno River. The sequence, from top to bottom, consists of an upper layer of topsoil and a thin predominantly sandy layer, which contains a shallow and ephemeral water table with limited productivity. The thickness of these permeable layers varies between 1.00 and 1.50 meters. The substrates immediately below are composed of silty clays transitioning to weakly sandy silts. The base of these limited aquifers consists of clayey or clay-peaty layers.

Below these layers, at approximately -14 to -16 meters below ground level, a sequence of pyroclastic rocks with intercalations of clayey layers transitions to grey-yellowish sands, constituting a deeper and more productive aquifer.

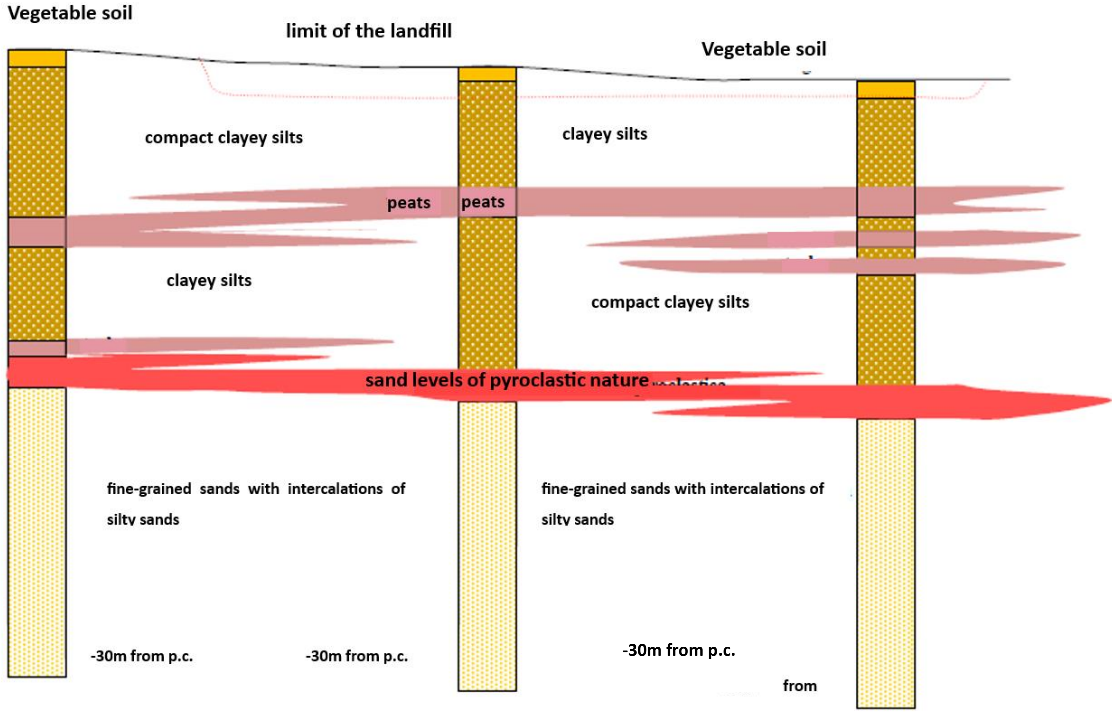


Figure 30: Lithostratigraphic reconstruction below the So.Ge.Ri landfill.

6.4 Description of state of fact of the site

The Bortolotto-Sogeri large area is located in the northeast sector of the main residential nucleus of Castelvolturno (CE). It consists of the following components:

- "Bortolotto" landfill: This publicly managed landfill operated by the CE4 Consortium was used for the disposal of municipal solid waste (MSW) from 1995 to 2005. It covers an area of approximately 4.5 hectares and has an estimated volume of around 400,000 cubic meters.
- "So.Ge.Ri." landfill: This privately managed landfill operated by the eponymous company was used for the disposal of MSW in the 1980s and 1990s. It covers an area of approximately 12 hectares and has an estimated volume of around 1,100,000 cubic meters.
- Additional land: Approximately 110,000 square meters of land with predominantly agricultural use were included to complete the large area.

Large areas typically comprise two or more waste disposal sites, and over time, various investigations, mainly focusing on the groundwater, have revealed contaminations potentially related to poor site management. In other words, these are relatively small portions of land where available environmental data suggest that the environmental situation may be particularly compromised due to the simultaneous presence of multiple contaminated or potentially contaminated sites.

The absence of post-operational management for the two landfills has resulted in past occurrences of leachate leakage from the landfill bodies, impacting both the groundwater and surface water bodies, as well as the adjacent agricultural fields. It should be noted that leachate can flow into the stormwater drainage channel and eventually reach the sea through the Agnena Canal.

The following remediation activities are currently ongoing within the large area: a) Regarding the "Bortolotto" landfill, the monitoring of environmental matrices is in process by the operator (GISEC Srl); b) Interventions are being carried out on the "So.Ge.Ri." landfill by SOGESID as the implementing entity of the Environmental Compensation Agreement; c) The agricultural areas adjacent to the landfills are being investigated and evaluated by the institutional working group "Terra dei fuochi."

The purpose of the characterization activities in the large area is to complete the characterization, which needs to be properly calibrated for the areas that have not yet been investigated.

The area subject to environmental characterization includes the agricultural areas of the large area, covering approximately 11 hectares, and the "Bortolotto" landfill site, covering approximately 4.5 hectares, for a total of 15.5 hectares. The "So.Ge.Ri." landfill site is excluded from the characterization.

Access to the large area is ensured by taking SP 161 towards the sea-inland direction. From this SP, there is a common gate that provides access to a road solely serving the two landfills.

6.4.1 State of fact of “Bortolotto” landfill

In the southeast sector of the Bortolotto-Sogeri large area, there is the former publicly managed landfill known as Bortolotto, used for the disposal of municipal solid waste (MSW). During several site visits to the investigated sites, with prior authorization from the personnel of the CE/4 Consortium responsible for landfill management, the current state of the sites was defined. The Bortolotto landfill has a raised cultivation structure with multiple levels, reaching a total height of approximately 21 meters. The entire site is enclosed by a metal fence, and access to the facility is provided through a sliding steel gate located on the common access road for the landfills. From the base of the landfill, there is access to the top of the cap via a dirt service track.

Preliminary documents obtained before the start of the service indicate that an estimated volume of approximately 400,000 cubic meters of waste was deposited in the landfill between 1995 and 2005. The surface area of the landfill and the adjacent areas is approximately 4.5 hectares.

The existing knowledge is based on geophysical surveys conducted by the CE4 Consortium, which indicate that "the waterproofing system is continuous and homogeneous across the entire landfill area," and preliminary environmental investigations carried out in 2006 by the Municipality of Castel Volturno as part of the Campania Regional Operational Program 2000-2006 – Measure 1.8 DGR No. 400 of 28/03/2006 [46].

During the site visit, the presence of a bentonite liner placed beneath the first terrace and folded over the perimeter ditch was confirmed at the Bortolotto landfill. The landfill also exhibits widespread vegetative cover consisting of spontaneous vegetation and medium to tall shrubs (Figure 31). Aerial drone surveys have shown the existence and functionality of the stormwater management network, which includes gutters, manholes, and drainage ditches that channel rainwater from the top of the landfill to its base.

Surrounding the cultivation basin is a well-maintained perimeter service track made of stabilized material. There are no stagnant water areas, bumps, or depressions, making easy the access for operational vehicles. Primary technological facilities for a controlled landfill are present, including leachate collection wells, biogas capture wells with a static flare, and lighting systems. However, during the site visit, the actual functionality of these facilities could not be confirmed.

Figure 31: 3D view of the Bortolotto landfill - Aerial shot of 10/28/2021.You can observe the high grassing of the cap and the planting of numerous medium-sized trees.

7 Historical reconstruction of activities conducted on the site

7.1 Summary of the CP carried out for the So.Ge.Ri landfill (2017-2018)

A total of 30 boreholes were drilled to a depth of 7 meters below ground level (m bgl). These boreholes were distributed along the perimeter of the landfill site and in the external agricultural areas, in accordance with the approved Characterization Plan and the Definitive Project prepared by Sogesid S.p.A. Three boreholes were deepened to 7.5 m bgl in consultation with ARPAC (Campania Regional Agency for Environmental Protection), as prescribed in the minutes of Technical Meeting No. 47/TF/16 held on November 10, 2016, at the ARPAC provincial department in Caserta. From each borehole, three soil samples were collected from specified depths: 0-1 m bgl (C1), 3.5-4.5 m bgl (C2), and 6-7 m bgl (C3). The samples were catalogued and stored accordingly.

During the drilling process, which was performed dry using a CMV MK 600 drilling machine and adequately decontaminated equipment between each borehole, Photoionization detector (P.I.D.) measurements were taken to determine the in-situ concentration values of Volatile Organic Compounds (VOCs). Boreholes were also conducted for sampling the waste materials, which were subjected to basic chemical characterization analysis, leaching tests, and geotechnical tests. These boreholes were conducted within the landfill body. From these boreholes, three reworked samples (C1 = 2-4 m bgl, C2 = 7-9 m bgl, C3 = 12-14 m bgl) and three undisturbed samples (ci1, ci2, ci3) were collected. Three boreholes were further drilled and deepened to a depth of 25 meters below ground level (m bgl) to install "open tube" piezometers made of non-toxic PVC with a diameter of 4”. Protective wells were also installed above the piezometric tubes (drivable).

Furthermore, the following samples were collected:

- 6 leachate samples (collected from the internal perimeter channels within the landfill and transported to the collection basins located in the SE, NE, and NW corners of the landfill) for characterization.
- 12 surface water samples collected from the perimeter channels for chemical and microbiological analysis. The concentrations of the sought analytes were compared with the limit concentration values expressed in Annex 1, Tables 1/A and 1/B of Decree No. 56/2009.

The investigations carried out in the Characterization Plan, according to Legislative Decree No. 152/06, at the So.Ge.Ri. landfill in the Bortolotto area of Castel Volturno (CE) have revealed the following results:

1. *The geometry and thickness of the waste deposit are clearly visible, characterized by average electrical resistivity values of r > 20-25 Ohm*m and an extensive dipolar magnetic anomaly oriented from South to North, centred in the upper part of the landfill, with the bottom of the deposit located on average about 2 meters below the pre-existing ground level.*
2. *The soils on which the waste was deposited (in embankments) consist of clayey and silty-clayey lithologies of fluvial-alluvial and palustrine depositional environments, with significant portions and even saturated thicknesses (water adsorbed to particles, capillary and film water), with resistivity values of 5 Ohm*m < r < 10 Ohm*m. These soils contain aquicludes, interspersed with sandy-silty lenses representing overlapped confined and/or semi-confined and pressurized aquifers (r < 5 Ohm*m). Within this alluvial layer, traces of ancient river meanders and/or agricultural drainage and hydraulic management channels (located on both the right and left banks of the Volturno River) can also be found.*
3. *The geoelectrical profiles show repeated entries of water into the waste, from the surface towards the interior of the landfill body, connected to the rather partial upper sealing, resulting in the formation of leachates that migrate laterally and downward. These leachates contribute both to the feeding of the perimeter leachate collection channels (which are not fully intact) and to the saturation of the underlying clayey soils.*
4. *Significant and distinctive evidence of presumed buried structures within the landfill body can be observed specifically in geoelectrical profiles G1 - G6. In these profiles, approximately starting at a distance of 120 meters from the origin (south) and extending to a depth of about 5 meters and a width of 15-20 meters, the resistivity values are significantly higher (r > 5000 Ohm*m) than those of the surrounding waste.*
5. *Dipolar magnetic anomalies in a north-south (S-N) orientation, defined through the interpretative analysis of CMT (Continuous Magnetic Testing) measurements and its vertical gradient, testify to the presence of scattered ferrous objects and clusters within the landfill body. There is clear evidence of one or two large inductive (S-N) dipolar anomalies centred in the northwest corner of the landfill, near the area where profiles of high chargeability and presumed buried structures were detected by geoelectrical tomography investigations, as well as several other small significant anomalies as depicted on the dedicated map.*
6. *The numerous magnetic anomalies oriented differently from the S-N direction are instead associated with various sub-surface pipelines, often consisting of metallic components,*

running along the planes and slopes of the landfill, as well as numerous diverse objects scattered on the surface.

7. *The resistivity of the landfill's foundation soils frequently indicates very low values, sometimes even below 1 Ohm*m, which can be attributed to high mineralization or salinity of the impregnating/saturating groundwater. This evidence could be related to the marine contamination present near the bed of the Volturno River and an extensive area on both the left and right banks of the river, from the river mouth to the town of Cancello Arnone. This contamination results in high electrical conductivity values of the groundwater in this area (1100 - 1400 mS/cm).*
8. *Due to repeated vertical and horizontal displacements of the CSL (Continuous Slotted Leachate) panels that make up the structures of the leachate collection and transport channels, and settlement in the foundation at various points of the flooring of these channels, there is a continuous leakage of leachate outward into the external lateral irrigation drainage channels.*
9. *The surface waters flowing in the aforementioned drainage channels are contaminated due to mixing with leachates, making their quality non-compliant with current regulations. In particular:*
    - *The surface waters sampled along the South Canal are of good quality, as they comply with the concentration limit values of D.M. 56/2009.*
    - *The surface waters sampled along the West Canal show concentration values slightly higher than the limit values of D.M. 56/2009 and, therefore, are non-compliant regarding the total Chromium and Nickel values.*
    - *On the other hand, the surface waters of the East and North Canals are significantly non-compliant with the limits established by tables 1/A and 1/B of D.M. 56/2009 for the parameters total Chromium, Nickel, and Lead, as well as very high concentrations of Ammoniacal Nitrogen (NH4), Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BOD5). These surface waters converge at the external northeastern corner before heading north and entering the Regio Canale Agnena, approximately 5 km away in a straight line. The deterioration in the quality state between the upstream and downstream portions compared to the landfill site, for each of the two irrigation drainage channels, is likely attributable to the mixing of surface waters with leachate flowing from the landfill site.*

10. *The subsurface soils in the investigated area are essentially compliant with the CSC as specified in Table 1 of Annex 5 to Part IV of Legislative Decree 152/06 and subsequent amendments, with the exception of a few exceedances of CSC in external agricultural soils for parameters such as Beryllium, presumably attributed to natural background levels, and for Arsenic and Cobalt in soils likely affected by agricultural practices that could produce these contaminants.*
11. *The groundwater samples collected at existing and newly established piezometers show exceedances of the CSC (Table 2 - Annex 5 - Part IV of Legislative Decree 152/06) for the parameter Manganese (Mn) at all sampled points and for Iron (in a piezometer located upstream in the hydrogeological context). It is important to note that these exceedances are attributed to natural background levels.*
12. *Lithostratigraphic characterizations and measurements of piezometric levels reveal the presence of a deep confined or semi-confined aquifer (located in the sands between approximately 8 and 11-12 meters below ground level) that, during the high-water period, rises in pressure in the existing piezometers to nearly ground level. It is characterized by a low-gradient flow with an east-west direction that during the low-water period locally seems to reverse, allowing a more significant inflow and outflow of seawater into the more permeable lithologies and the main aquifer.*
13. *The very low permeability, measured in situ (from 10^{-7} to 10^{-8} m/s), of the surface clayey and clayey-silt lithotypes found at the base of the landfill and laterally adjacent to it, as well as those extending up to the top of the sandy aquifer, prevents the downward drainage of leachate and the associated contaminants. Instead, they accumulate within the landfill body and then seep out laterally into the leachate channels, and subsequently into the external irrigation drainage channels, contaminating only the surface waters.*

7.1.1 Summary of the investigations carried out in the Bortolotto landfill

Preliminary investigations carried out in 2006 by the Municipality of Castel Volturno as part of the Campania 2000-2006 Regional Operational Programme – Measure 1.8 DGR no. 400 of 28/03/2006 [46] revealed exceedances of CSC in groundwater for Arsenic, Chromium, Iron, Manganese, Nickel, Lead, Zinc, Benzo(g,h,i)Perylene, 1,2-Dichloropropane, and Total Halogenated Organic Compounds. Analyses of water samples taken from monitoring wells in 2004 indicated exceedances for Iron, Manganese, and Arsenic. Subsequently, further analyses revealed exceedances of CSC for Chlorides, Sulphates, Copper, Mercury, Nitrates, and Ammonium.

8 Preliminary conceptual model of the site

In this chapter, basic information about the site under characterization is presented, including potential sources of contamination, migration pathways, and exposure pathways considered based on the results of environmental investigations for the characterization of the SO.GE.RI. landfill and the surrounding areas.

The Preliminary Conceptual Model, defined in Annex II to Part IV of Legislative Decree No. 152/06, is the technical tool that guides the definition of the investigation plan, in which the following aspects are related:

- Sources of contamination
- Migration pathways of contamination sources
- Targets of contamination.

It is developed based on historical information available before the start of the investigation plan, as well as investigations conducted in various environmental matrices during the preliminary site investigation campaign. The preliminary conceptual model describes specific site characteristics in terms of potential contamination sources, the extent, characteristics, and preliminary quality of environmental matrices influenced by the presence of existing or past activities conducted on the site, and potential migration pathways from contamination sources to identified targets. This model must be developed before conducting field activities to guide the definition of the investigation plan.

An integral and fundamental part of the site's conceptual model is the preliminary definition, based on available historical information, of the hydrogeological characteristics of shallow and deep aquifers as potential pathways for contamination.

In the following flowchart (Figure 32), the elements of the considered conceptual model are summarized in a general manner. The flowchart provides a general conceptual model of a contaminated site, including contamination sources, migration pathways, and possible exposure pathways.

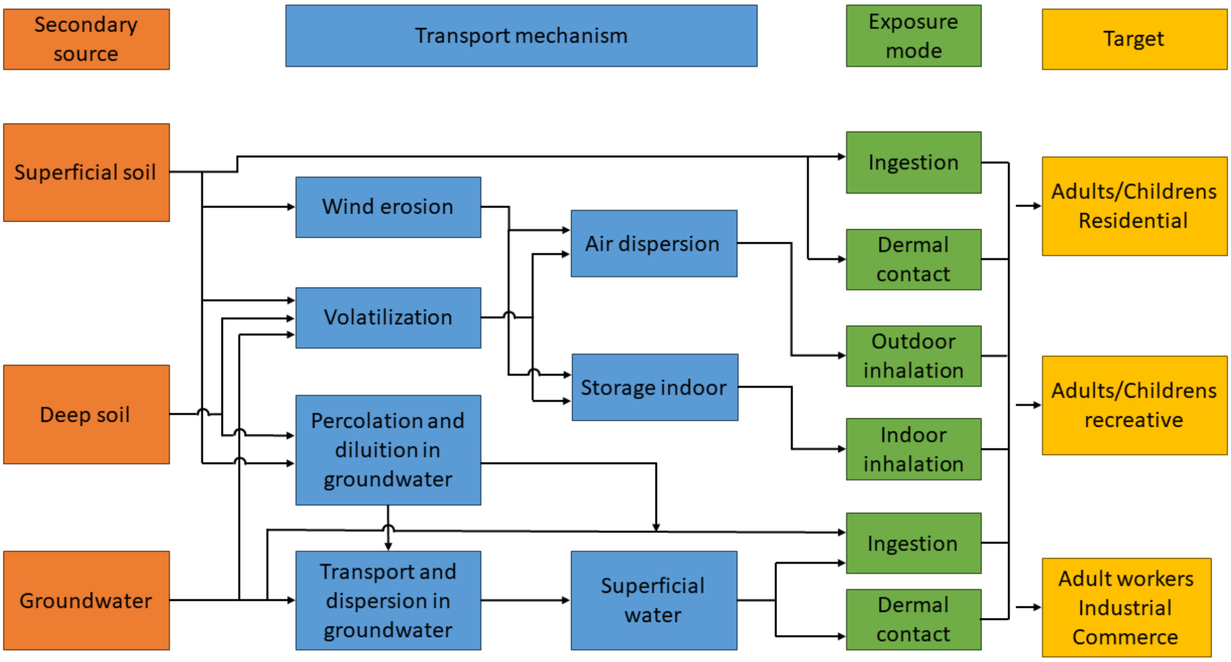


Figure 32: Schematization of site's conceptual model

8.1 Primary source of contamination

The primary source of contamination is the waste disposal of the So.Ge.Ri. and Bortolotto landfills, which cover an area of approximately 17 hectares. The landfill is characterized by several distinct cultivation lots, with heights reaching up to 21 meters above ground level (p.d.c.). Based on acquired historical documentation, it is estimated that around 1,400,000 cubic meters of municipal solid waste (MSW) have been deposited in the cultivation basins.

The main emissions associated with the deposition of municipal solid waste in conventional landfills are leachate and biogas. In particular, it is possible that over the years, there have been infiltrations of rainwater into the landfill body, and this water has had the opportunity to percolate through the waste, transforming what reached the ground into not just meteoric water but actual leachate.

The lack of detailed information on landfill management practices and waste deposition methods that occurred over the years, as well as the exact type of waste disposed of, makes the issue of leachate infiltration into the subsurface particularly complex.

Relative to the different permeability characteristics of the deposited waste, it is possible that preferential migration pathways for groundwater and infiltrating rainwater have indeed formed within the waste body. This circumstance leads to the following two valid considerations:

- It is plausible that pockets of leachate may have formed within the waste body if fluid threads encountered substrates with low permeability.
- It is not possible to determine with certainty the migration path of the fluid threads within the waste body.

A similar discussion can be developed in parallel with reference to biogas. It is known that the permeability characteristics of soils also have implications for the migration of gases within the interstitial spaces that characterize soils.

Clays or, in general, compacted soils with similar permeability characteristics strongly hinder the migration of gases in the soil and, when not fractured or disturbed, are virtually impermeable. Soil moisture reduces gas phase permeability because the water adhering to solid particles and that trapped in voids can impede gas flow. Depending on site-specific conditions, other factors may also interfere with gas migration in the soil. These factors can include karst or tectonic fracture systems, the root systems of trees and shrub vegetation, and boundaries between different types of deposited materials.

While, on one hand, the factors listed above contribute to the creation of preferential pathways for gas migration in the subsurface, it is also true, on the other hand, that the presence of potential low-permeability layers, pavements (which does not apply to the current study), and pockets of liquids like leachate can impede gas migration in the subsurface.

These considerations make it reasonable to suspect, in addition to what has already been mentioned, the presence of pockets of biogas within the waste body.

8.2 Secondary source of contamination

The secondary source of contamination is identified within the environmental compartment subject to contamination. Regarding the secondary source of contamination, this can be found in:

- Deep unsaturated and saturated soil.
- Groundwater and surface water, which, although not intended for drinking purposes, are considered to have established intensive use in agriculture and for livestock watering.

8.3 Transport mechanisms

The possible migration pathways that are potentially active on the site for the identified contamination sources are listed below:

For Soil: volatilization and percolation into the groundwater.

For Groundwater: transport and dispersion of contaminants within the groundwater.

The main transport modes from primary sources to secondary sources can be identified as follows:

- Leachate emissions into the environment due to seepage from the bottom and lateral surfaces of the Bortolotto landfill.
- Surface runoff of contaminated water towards the surrounding agricultural lands.
- Gas emissions into the air due to the limited efficiency of the biogas collection system and/or migration phenomena.
- Biogas or biogas condensate emissions due to potential losses in the collection system.

8.4 Exposure modes and contamination targets

Through transport mechanisms, primarily volatilization and percolation into the groundwater, contaminants reach the target, which comes into contact with toxic or carcinogenic chemical species through exposure pathways. Typically, the exposure pathways that characterize contaminated sites include:

- Ingestion of drinking water.
- Ingestion of soil.
- Dermal contact.
- Inhalation of outdoor vapors.

Exposure pathways and modes are the means by which the potential target comes into contact with contaminating chemical species. Direct exposure occurs when the exposure pathway coincides with the contamination source, while indirect exposure occurs when the receptor's contact with the pollutant occurs as a result of its migration and, therefore, happens at some distance from the source. In the case of the Bortolotto landfill, it is believed that target exposure occurs indirectly through the ingestion of drinking water, dermal contact with the contaminated matrix (soil or water), or outdoor inhalation of contaminants.

Through the exposure pathways, the primary targets generally considered are only human receptors. The potential targets exposed to the spread of contamination, through the described exposure pathways, have been selected based on the urban planning designation of the site and are identified as follows:

- Adult occasional workers on-site.
- Adult and child residents off-site.
- Groundwater resource.
- Surface waters (Volturno River and Agnena Canal).

Another possible source of pollution could be the potential biogas, which can be transported into the surrounding environment by atmospheric agents (wind).

8.4.1 Resident population potentially exposed

The Bortolotto landfill area is located in an area with very low population density. Specifically, there are no residential settlements within a radius of 1500 meters from the site boundaries.
The nearest significant cluster of houses is located along the coast at approximately 4.5 kilometers to the west, while the center of Castel Volturno is about 5 kilometers to the south. Other relatively nearby populated centers are Cancello and Arnone, situated approximately 5 kilometers to the east, and Mondragone, located about 8.5 kilometers to the northwest, in a straight line.

8.4.2 Non-resident population potentially exposed

The exposed non-resident population is essentially composed of:

- Temporary workers employed in the MISP activities of the So.Ge.Ri. landfill.
- Occasional workers involved in the post-operative management of the Bortolotto landfill owned by the CE/4 Consortium.
- Agricultural workers on the agricultural lands within the Bortolotto landfill area.

There are no other types of workers potentially affected by contamination in the area under consideration, as there are no industrial or commercial activities of any kind present.

8.4.3 Natural targets of interest for the food chain

The natural targets of relevance for assessing the induced risk through the food chain can be identified as:

- Buffaloes and their derived products.
- Forage production.
- Horticultural and fruit production.

8.5 Preliminary considerations on the hydrogeological flow model

As described in the paragraphs above, following the execution of the characterization plan for the So.Ge.Ri. landfill and historical studies conducted, it is possible to reconstruct lithostratigraphic characteristics and measure piezometric levels in the vicinity of the Bortolotto area. This reconstruction may be considered approximate since the isopiezometric structure is based on five piezometers: two in the hydrogeological valley, other two upstream of the hydrogeological area and one located at the south-central perimeter of the landfill.

Nevertheless, this does not preclude the possibility of making some important considerations.

The flow models reveal the presence of a deep confined or semi-confined aquifer (aquifer present in the sands located approximately 8 to 11-12 meters below the ground level) that, during the wet season, becomes pressurized, rising in the monitoring wells almost to ground level. This aquifer exhibits a low-gradient flow with an east-west direction. During the dry season, it appears that there may be some local reversal of flow, allowing a more significant inflow of marine waters into the more permeable lithologies and the main aquifer (Figure 13).

This could be due to the low groundwater and surface water inputs during the period from March to late June of this year, resulting in the cancellation of the surface water contribution from the reclamation/filling area, a significant reduction in groundwater flow volumes originating from the surrounding mountainous areas of the Volturno plain, and a prevalence of seawater inputs (essentially a local and substantial flow reversal, which could also explain the significantly increased conductivity).

In order to define the final conceptual model of the site with greater certainty, particularly regarding the direction of hydrogeological flow, the proposed plan aims to install a greater number of monitoring wells distributed around the perimeter of the area of interest.

8.6 Planning of the investigation campaign for the Bortolotto-Sogeri large area (CE)

The aim of the proposed characterization plan is to complete the investigations previously carried out by SOGESID on the "Bortolotto" Large Area.

Specifically, the objectives are:

- Define the contamination framework for areas of the site that have not yet been investigated, allowing the advancement of the reclamation process under Article 242 of Legislative Decree 152/2006 [14].
- Enhance the base knowledge through further investigations, with the goal of obtaining valuable information to supplement the environmental data acquired from other sites.

The investigations will involve the environmental characterization of **soil, subsurface, water environment** (groundwater and surface water**), waste, leachate, and the atmosphere**.

The following are the activities scheduled:

- Execution of 47 soil borings within the investigation zone, which is 50 meters wide and adjacent to the perimeter of the landfills. These borings will be distributed in a regular grid pattern with approximate dimensions of 50 meters by 50 meters. The purpose is to collect soil samples for chemical analysis. Fifteen of these borings will be equipped with piezometers to intercept the groundwater.
- Sampling and analysis of groundwater, with one sample taken from each installed piezometer (total of 15 samples).
- Sampling and analysis of surface water (10 samples) located along the perimeter channels of the two landfills in question.
- Sampling and analysis of waste: eluate release test (total of 16 samples).
- Sampling and analysis of waste: respirometric index (total of 2 samples).
- Sampling and analysis of leachate (total of 11 samples).
- 2D electrical resistivity tomography.
- Air quality monitoring near the waste deposit area (total of 20 monitoring stations).
- Permeability tests and geotechnical physical analysis.

- Determination of site-specific parameters aimed at implementing a potential site-specific risk analysis.

Although the preliminary project document indicates a drilling depth of 20 meters for simple boreholes and 30 meters for boreholes equipped with piezometers, given the historical studies taken into account, it is considered sufficient to extend the simple borehole drilling to the depth of the water table interception (estimated at approximately -15.0 meters from the ground surface). The soil sampling should not penetrate the saturated soil layer. On the other hand, piezometers will be drilled to a depth of approximately 25.0 meters from the ground surface, which is sufficiently below the piezometric level observed during the environmental characterization of the So.Ge.Ri. landfill (maximum of about 13-15 meters).

Regarding the number of samples to be taken for each borehole, three samples will be collected at different depths in accordance with the current regulatory framework and technical guidelines for project bidding.

8.7 Soil and subsoil characterization

The choice of the number of boreholes, their location, and the number of samples, already established in the specific technical specifications of the tender document, is made in accordance with the "Guidelines for Technical Procedures for Interventions" - Appendix 2 to the update and adaptation of the Regional Plan for Environmental Remediation of the Campania Region (Regional Decree No. 35 of January 29, 2019 [47]). These guidelines provide general guidance for the characterization of contaminated sites, with reference to the location of sampling points and their number. It is recommended to adhere to the provisions of the "Manual for Environmental Investigations in Contaminated Sites" (APAT 2006) [48], which provides indications regarding the minimum number of boreholes based on the size of the site, as highlighted in the following table:

Table 11: Number of surveys for characterization according to the size of the site

Site surface (m^2)	Sampling points
< 10.000	At least 5 points
10.000 – 50.000	from 5 to 15 points
50.000 – 250.000	from 15 to 60 points
250.0 – 500.000	from 60 to 120 points
> 500.000	At least 2 points every 10.000 m^2

With reference to each environmental matrix (soil, subsurface, and groundwater), the choice of the location of sampling points can be based on:

- Historical data available and all information synthesized in the preliminary conceptual model, in the case of a complex site where vulnerabilities are already known, and available data allow the construction of a conceptual model (reasoned location).
- A predefined or random grid, in the case of sites for which there is no historical information to establish a preliminary conceptual model (systematic location).

In this case, the determination of the sampling grid is based on local knowledge and site-specific constraints. The "Area Vasta" is characterized by agricultural land, areas restricted for agricultural and silvo-pastoral production, and areas within the Bortolotto landfill not affected by waste disposal.

8.7.1 Characterization of soils located within the prohibition zone for the use of agricultural land and within the perimeter of the Bortolotto landfill

Consistent with the guidelines of the Manual for the Characterization of Contaminated Sites, which defines the minimum number of boreholes to be conducted based on the site's extent, 47 boreholes will be carried out along the perimeter of the Bortolotto landfill and in the surrounding areas that characterize the large area.

As it is a site with a known nature (landfill), and the objective of this characterization plan is to provide an understanding of the potential impacts generated by the landfill on the surrounding environment and its possible contamination status, the boreholes are primarily located in the agricultural lands adjacent to the landfill sites. This approach will allow the characterization of environmental matrices and determine if the presence of the landfill has had any repercussions in terms of pollution.

Furthermore, since there are two different landfills with different operators and cultivation periods, perimeter boreholes around the Bortolotto landfill have been planned, located within the cadastral perimeter but outside the waste cap, with the aim of identifying the possible presence of buried waste beyond the known boundaries and locating the source of any contamination by understanding the groundwater flow patterns. Based on the available information, simple soil boreholes for characterization will reach a maximum depth of 15 meters from ground level.

Regarding the sampling, in accordance with sector-specific regulations, soil characterization will focus only on the unsaturated zone unless there is an accumulation of waste in the saturated zone or unless different directives are given by the Control Authorities.

Concerning the number of samples to be taken for each borehole, reference is made to Annex 2, Part IV - Title V of Legislative Decree 152/06 [14] and the "Manual for Environmental Investigations in Contaminated Sites APAT 43/2006 [48]," which specify that for each borehole, samples should be collected as follows:

- Sample 1: From 0 to -1 meter from the ground surface.
- Sample 2: 1 meter to include the capillary fringe zone.
- Sample 3: 1 meter in the intermediate zone between the two previous samples, plus the collection of 14 topsoil samples.

Out of the 47 planned boreholes, 15 will be converted into open-tube piezometers and will be drilled to a depth of 25.00 meters below ground level, taking into account the experimental field data for the characterization of the So.Ge.Ri. landfill site, as documented. After the drilling phase is completed, precise location and elevation surveys of the drilling points will be conducted.

At the end of the investigation phase, the drilled boreholes will be properly sealed to prevent the creation of preferential contamination pathways and to maintain the current state of the system.

The results of the soil sample analyses will be compared with the Contamination Threshold Concentrations listed in columns A and B of Table 1 in Annex 5, Title V of Part IV of Legislative Decree No. 152 of 2006 and subsequent amendments. Specifically, for the land parcels outside the landfill, reference will be made to column A (Sites for Public, Private, and Residential Green Spaces), while for the soil samples located within the boundaries of the parcels pertaining to Bortolotto, the reference concentrations will be based on column B of the same table (Commercial and Industrial Sites).

8.7.2 Soil chemical analysis

The Legislative Decree 152/2006 [14] and subsequent amendments provide a series of analytical determinations for soils (Table 1, Annex 5, attachments to Part IV) to be carried out on site samples. During the analysis, the following conditions will be ensured:

- Execution of the analysis in compliance with the holding times of the methods and field stabilization where necessary.
- Conducting the analysis according to officially recognized and ISO 17025 accredited methods as appropriate, with the application of QA/QC protocols required by regulations and industry practices.

The complete list of parameters to be analysed for various environmental matrices characterized during the investigation phase, along with the standard methods to be used for extraction and analysis, is provided in the appendix unless otherwise specified by the regulatory authorities.

Additionally, the sampling of 14 topsoil samples is planned, representing 10% of the samples plus three control samples. The following analyses (Table 12) will be performed on these samples in accordance with the technical specifications of the tender:

Table 12: Parameters and methods for topsoil characterization

Topsoil analysis with reference to Legislative Decree 152/2006 Table 1, Annex 5, part IV	
Parameter	Analysis and extraction method
Dioxins and furans	EPA3546 2007 - EPA 8280B 2007
PCB	UNI EN 17322 2020
Asbestos	M.U 1978:06

The reference analytical package is derived from the PPD (Preliminary Planning Document) taken into account at the outset, which has been calibrated based on the available historical data. However, it should be emphasized that, during the approval of the Plan, different analytical sets, as well as analysis methods, may be agreed upon with ARPAC (Regional Environmental Protection Agency), and these will be reviewed in accordance with the Contracting Authority.

Regarding the adversarial investigations, during the implementation of the Plan, samples equal to 10% of the total (sums provided in the economic framework) will be collected. It will be the responsibility of the RTI to transmit the executive operational schedule of the samplings well in advance, so ARPAC can be informed in a timely manner of the sampling date.

In order to determine whether exceedances of CSCs have occurred, the results of soil sample analyses will be compared with the Threshold Concentrations of Contamination listed in columns A and B of Table 1, Annex 5, Title V of Legislative Decree No. 152/2006 [14] and subsequent amendments, with reference to the specific urban planning land use provisions.

Specifically, for soil lots outside the landfill but located within the restricted area, reference will be made to column A (Sites for public, private, and residential Green use). For soil samples located within the boundaries of the Bortolotto landfill parcels, reference concentrations will be related to column B of the same table (Commercial and Industrial use Sites).

8.8 Groundwater characterization

To characterize the groundwater quality and evaluate its piezometric level, it is planned that fifteen out of the total 47 boreholes will be equipped with piezometers.

Upon completion of the piezometer installation phase, they will be sealed, and locks will be placed to make them suitable for future fixed monitoring points.

Regarding the sampling, in this specific case, it will be carried out using stainless steel samplers equipped with mechanically operated head valves and bottom valves, as specified in the tender technical specifications. The locations of the piezometers are represented in the appendix 1.

8.8.1 Groundwater chemical analysis

In the appendix 1, you can find the parameters to be analysed during the investigation phase. During the implementation of the Plan, samples for cross-checking will be collected, amounting to 10% of the total (as specified in the economic framework), and ARPAC will be notified well in advance of the sampling date.

To determine whether there have been any exceedances of the Concentrations Thresholds of Contamination (CSC), the results of the groundwater samples' analyses will be compared with the Contamination Threshold Concentrations listed in Table 2, Annex 5, Title V of Part IV of Legislative Decree No. 152 of 2006 [14] and subsequent amendments.

8.9 Waste characterization

In order to determine the merchandise nature and classification of the waste, a total of 16 samples will be collected from the waste within the "Bortolotto" landfill. Specifically, these samples will be taken from eight pit/trench excavations with a depth of approximately 2.00 meters, carried out using small mechanical equipment in the landfill's plains and slopes. The samples collected will represent both the first and second meters of the excavation.

All samples will undergo leachate release tests in accordance with Annex 4 of Legislative Decree No. 121 dated September 3, 2020 [15].

Considering the significant time period between the closure of the Bortolotto landfill and the preparation of the characterization plan and given that the waste matrix can now be considered inertized/stabilized, it is deemed sufficient to perform only 2 tests to assess the respirometric index (RI).

8.10 Surface water characterization

In accordance with Ministerial Decree of April 14, 2009, No. 56 [49], titled "Technical Criteria for Monitoring Water Bodies and Identifying Reference Conditions for Amending the Technical Rules of Legislative Decree No. 152 of April 3, 2006, on Environmental Regulations, Prepared Pursuant to Article 75, Paragraph 3, of the Same Legislative Decree," and in concurrence with the analyses conducted in 2017 for the characterization of the SO.GE.RI. landfill (Document "Results of the Implementation of the Characterization Plan Approved by Regional Directorate Decree No. 130 of October 18, 2016 [50]" for the Emergency Safety Measures of the SO.GE.RI. s.r.l. Landfill in the Bortolotto Area), and following the indications of the tender specification, the parameters to be obtained through the analyses of surface water samples have been selected (as listed in the appendix).

Analyses will be carried out on 10 (ten) surface water samples, plus three control samples, collected from external and perimeter irrigation drainage channels around the site.

Chemical and microbiological analytical determinations will be conducted on these surface water samples, and the concentration values of the sought analytes will be compared with the limit concentration values provided in Annex 1, Tables 1/A and 1/B of Ministerial Decree No. 56/2009 [49]. This comparison will allow an assessment of whether there has been an improvement in the overall environmental quality of surface water as a result of the ongoing remediation efforts.

It should be noted that, in accordance with the opinion rendered during the service conference on March 22, 2022, by the “Consorzio Generale di Bonifica del Bacino Inferiore del Volturno” (General Consortium for the Lower Volturno Basin Reclamation), in order to avoid any potential interference with the underground conduits of the irrigation distribution network that constitute the right bank of the Volturno (see the attached maps in the appendix 1), activities related to the sampling of surface water will require explicit authorization to access construction sites and workplaces (Article 47 of the Hydraulic Police Regulations).

In the appendix 1, you can find the parameters to be analysed during the investigation phase.

8.11 Leachate characterization

The leachate characterization is necessary to assess the conditions of surface waters because there have been past incidents of leachate discharge into the perimeter channels around the Area Vasta, causing contamination. Although the planning document initially specified 20 leachate samples, it is considered sufficient to estimate 11 (eleven) leachate samples to be collected (plus three control samples) in the first instance. This decision is based on the fact that the old leachate collection and management channels around the SO.GE.RI. landfill (East channel, West channel, South channel) has been sealed following the implementation of the ongoing remediation measures and are therefore not considered useful for sampling.

Sampling will be conducted from the leachate collection tank of the Bortolotto landfill, from two leachate extraction wells within the same landfill, and, as proposed during the service conference, from leachate collection points located around the SO.GE.RI. landfill (a total of 8 sampling points).

8.11.1 Leachate chemical analysis

In order to make a comparison with the quality of surface waters, in accordance with the previous analyses conducted during the Characterization of the SO.GE.RI. landfill for the emergency safety project of the same, specific parameters (as listed in the appendix) for basic characterization have been selected. In the appendix 1, you can find the parameters to be analysed during the investigation phase.

8.12 Monitoring of air quality near the waste disposal

Such field analyses will be carried out using state-of-the-art portable equipment. In particular, a portable Photoionization Detector (PID) with high sensitivity will be used, which is a non-destructive instrument commonly used for detecting Total Volatile Organic Compounds (VOCs).

With this detector, the measurement is performed when the gas flows into the detector's chamber, which ionizes it through ultraviolet radiation from a lamp with specific energy. The ions, attracted to an electrode, generate a current proportional to the gas concentration.

To complement and complete the field measurements, which will be 15 in total, appropriate laboratory analyses will be conducted to characterize 5 samples for the parameter of Volatile

Organic Compounds (VOCs). This will provide a more accurate qualitative and compositional characterization of the collected soil gases.

8.13 Geotechnical investigations

The present plan also includes specific geotechnical investigations aimed at the physical characterization of the site's soils, including:

a) Geotechnical boreholes: 4 boreholes drilled to a depth of -20.0 meters below ground level.
b) Sampling of undisturbed soil: 3 samples for each investigation point plus three control samples, totalling 15 samples.
c) Laboratory permeability test under constant load in a permeameter, including saturation, for the fifteen samples collected in point b.
d) In-hole permeability tests during the construction of the piezometers: 15 tests.
e) Determination of the organic content for the fifteen samples collected in point b.
f) Laboratory geotechnical analysis for the physical-mechanical characterization of the soils, including:

- Grain size analysis for all environmental investigation samples and samples from point b (total of 180 samples).
- Determination of the percentage passing through sieve No. 200 and ASTM sieves No. 200 (0.075 mm), 40 (0.42 mm), and 10 (2 mm) according to ASTM D1140 standards for all samples (total of 180 samples).
- Determination of liquid limit and plasticity limit jointly for 180 samples.
- Natural unit weight, specific weight, and moisture content.
- Consolidation edometric tests to be conducted on 12 soil samples plus 8 waste samples.

8.14 Indirect investigations – 2D tomographies

The 2D electrical resistivity tomography (ERT) allows for the reconstruction of the subsurface structure based on measurements of soil resistivity, induced polarization (I.P.), and chargeability. 2D electrical resistivity tomography in alternating current (AC) enables the creation of 2D resistivity sections using a series of electrodes positioned on the ground and connected to a digital cable attached to a georesistivity meter (Figure 33). The georesistivity meter is capable of injecting current (I) and measuring potential differences (V) between predetermined quadrupoles. The obtained resistivity values can be correlated with various lithologies present in the subsurface or specific markers.

A geophysical survey using electrical resistivity tomography (ERT) is planned to be conducted on the top part of the landfill to identify and locate any concentrations of biogas and/or leachate. These indirect investigations will be carried out chronologically before the execution of direct investigations and interstitial gas sampling.

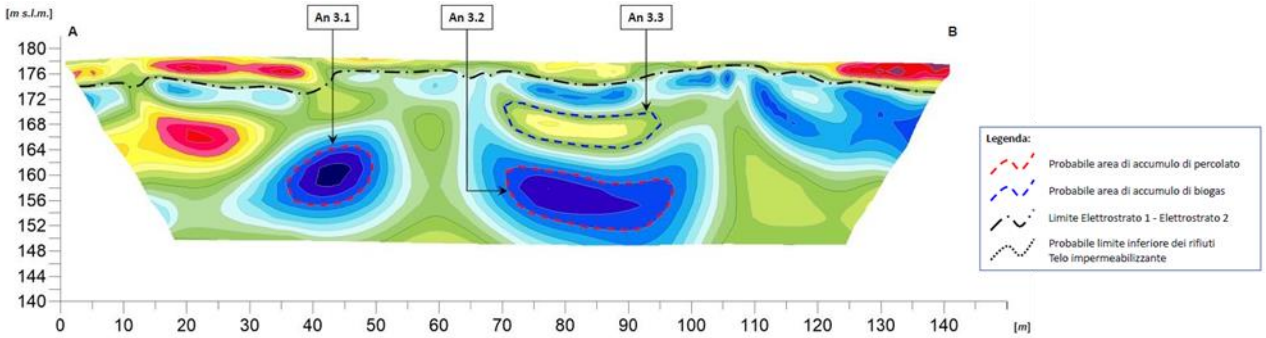


Figure 33: Example of tomographic restitution for a landfill survey

In the present case, a total of 9 survey lines are planned on the landfill, arranged along the longitudinal axis, plus two closed rectangular tomographies that encircle the sides of the landfill, as shown in table EG.09 in the appendix 1.

The total length of the survey lines is 3,700 meters.

9 Site specific parameters

The actual contamination status of a site, as mentioned in the introduction, involves defining the CSR, which are determined through a risk analysis if there has been a surpassing of CSC for any contaminant. Due to the site-specific nature of the potential risk analysis, the determination of CSR will depend on a set of site-specific parameters.

These parameters will be exclusively determined through direct verifications and/or investigations, following what is stated in the APAT note prot. 009462 of March 21, 2007. This note was shared within the APAT-ARPA-ISS-ISPESL working group and was acquired by the Ministry of the Environment and Protection of Land and Sea under prot. 8242/QdV/DI dated March 26, 2007.

It is well-known that the application of Level 2 risk analysis (site-specific) differs from Level 1 risk analysis (generic site) precisely because it uses site-specific parameters rather than default ones. Specifically, it is necessary to use characteristic values of the site under study for parameters that, according to the sensitivity analysis outlined in Appendix N of the manual "Methodological Criteria for the Application of Absolute Risk Analysis to Contaminated Sites, Rev.2," have the greatest influence on the analytical equations underlying the risk analysis procedure concerning Transport Factors. These parameters essentially relate to the geometry and geological and hydrogeological characteristics of the contamination source in both saturated and unsaturated zones, characteristics of open and confined spaces, certain chemical and physical parameters of the soil, and wind speed.

Laboratory Geotechnical Analysis:

During the investigation campaign, some samples will be collected for laboratory geotechnical analysis aimed at defining the geomechanical characteristics, grain size distribution, natural moisture content, permeability, porosity, and specific weight of the samples taken for each of the lithologies encountered during the drilling phase. This choice was made to achieve a greater degree of knowledge regarding the lithostratigraphic characteristics of the site in order to conduct a site-specific risk analysis as per Legislative Decree 152/06.

Analysis of pH, Soil Density, and Organic Carbon Fraction (FOC):

The collection of 12 samples of the soil and subsoil environmental matrix is planned to monitor pH, the fraction of organic carbon (FOC), and the density of both saturated and unsaturated soil.

Analysis of the Permeability Coefficient (kd):

Hydraulic conductivity at saturation, or the permeability coefficient Ksat, is a measure that indicates the ability of saturated soil to transmit water. This parameter depends on pore geometry (texture and structure) and fluid properties, particularly viscosity and density.

Table 13 lists the complete set of 33 parameters, categorized based on their association with the environmental compartments: unsaturated soil, saturated soil, open environments, and confined environments.

The choice of which parameters to determine from this list and their actual values for the specific case will be determined concurrently with the site characterization. These decisions are interdependent on the results of the characterization itself.

In the specific case of characterizing the site within the Bortolotto Large Area, it is currently believed that the parameters identified as 30, 31, 32, and 33 in the list can be excluded. These parameters are relevant to potentially contaminated sites in indoor environments and are therefore not pertinent in this specific case.

Table 13: Site-specific parameters for the definition of any level II risk analysis (source: Reference document for the determination of the site-specific parameters used in the application of the risk analysis pursuant to Legislative Decree 152/2006)

n.	SYMBOL	PARAMETER	UNITY OF MEASUREMENT
UNSATURATED SOIL			
1	L_{GW}	Depth of the water plate	cm
2	h_v	Thickness of the unsaturated zone	cm
3	W'	Extension of the contamination source in the main wind direction	cm
4	S_w'	Extension of the contamination source in the direction orthogonal to the main wind direction	cm
5	A'	Source area (relative to the main wind direction)	cm^2
6	$L_{s\,(SS)}$	Depth of the top of the source in the surface soil relative to the p. c.	cm
7	$L_{s\,(SP)}$	Depth of the top of the source in the deep soil relative to the p. c.	cm
8	L_f	Depth of the bottom of the source relative to the p.c.	cm
9	d_s	Source thickness in the deep soil (unsaturated)	cm
10	d	Source thickness in the superficial soil (unsaturated)	cm
11	L_F	Subjacency of the aquifer relative to the top of the source	cm
12	ρ_s	Soil density	g/cm^3
13	I_{ef}	Effective infiltration	cm/year
14	f_{oc}	Organic carbon fraction in the unsaturated soil	g-C/g-soil
15	pH	pH of the unsaturated soil	adim.
SATURATED SOIL			
16	d_a	Aquifer thickness	cm
17	W	Extension of the source in the groundwater flow direction	cm
18	S_w	Extension of the source in the direction orthogonal to the groundwater flow	cm
19	A	Source area (relative to the groundwater flow direction)	cm^2
20	W'	Extension of the contamination source in the main wind direction	cm
21	S_w'	Extension of the contamination source in the direction orthogonal to the main wind direction	cm
22	A'	Source area (relative to the main wind direction)	cm^2
23	v_{gw}	Darcy speed	cm/year
24	K_{sat}	Hydraulic conductivity in saturated soil	cm/year
25	i	Hydraulic gradient	adim.
26	f_{oc}	Organic carbon fraction in the saturated soil	g-C/g-soil
27	pH	pH of the saturated soil	adim.
OPEN / CONFINED ENVIRONMENTS			
28	U_{air}	Wind speed	cm/s
29	A_b	Total surface area involved in the infiltration	cm^2
30	L_{crack}	Foundation/walls thickness	cm
31	L_b	Indoor volume and infiltration area ratio (RES. or IND.)	cm
32	L_T	Distance between the top of the source in the unsaturated soil and the foundations base	cm
33	Z_{crack}	Foundations depth	cm

9.1 Compliance point

In the Annex 1 to Title V of Part IV of Legislative Decree No. 152 of 2006, "General criteria for site-specific environmental health risk analysis," in the section regarding "Components of parameterized risk analysis," it is stated that the point of compliance for groundwater represents the hydrogeological downstream point of the source where the restoration of the original state (ecological, chemical, and/or quantitative) of the groundwater body must be ensured to allow for all its potential uses as provided for in the third and sixth parts of this decree. Therefore, in compliance with the general precautionary principle, the point of compliance should typically be set not beyond the boundaries of the contaminated site subject to reclamation, and the corresponding CSR for each contaminant should be set equivalent to the CSCs as described in Attachment 5 of Part IV of the decree.

For the site in question, considering the peculiarity of the landfill's shape and the direction of the groundwater flow (E-W), a preliminary identification of the compliance point can be made at the piezometer Pz1, pending the availability of precise field data.

10 Experimental part

10.1 Potentiometric titrations

The principle of potentiometric measurements is based on measuring the variation in electromotive force (EMF) between two electrodes immersed in a solution following the addition of a titrating reagent.

The two electrodes are as follows:

- Indicator or working electrode: This is an electrode with a variable potential, sensitive to changes in analyte concentration.
- Reference electrode: This is a reversible electrode with a constant potential.

Potentiometric measurements are carried out using a combined glass electrode, which contains both the electrodes and is selective to protons (H^+). This electrode is connected to a potentiometer, which measures the potential changes following each addition of the titrant.

Inside the combined glass electrode, there is a solution containing H^+ ions at a constant activity, while outside it is immersed in a solution with an unknown activity. These two solutions are separated by a glass membrane in equilibrium with the H^+ ions present in both solutions, and the measured potential difference is precisely due to the difference in H^+ activity in the two solutions (internal and external).

Up to a pH~11, the response of the glass electrodes to changes in pH is linear according to the Nernst equation and is described by the following equation:

$$E = E^{0'} - (0.05916)\log\frac{a_{H^+}(internal)}{a_{H^+}(external)} \quad (25°C) \qquad (10.1)$$

The term $E^{0'}$ encompasses two potentials:

- Asymmetry potential: This is due to the non-uniformity of the glass surfaces of the membrane in contact with the internal and external solutions. This non-ideal behaviour is corrected by calibrating the electrode using solutions with known pH values.
- Junction potential: This exists at the interface between the salt bridge and each half-cell and is caused by the different mobility of ions in solution. The unequal diffusion of these ions on either side of the junction surface results in a charge separation and, consequently, a potential difference.

10.1.1 Instruments

Potentiometric measurements were conducted using a potentiometric apparatus comprising an integrated Metrohm 809 Titrando potentiometer with a Metrohm 801 stirrer, an Orion combined glass electrode Ross 8102 (with an experimental resolution of 0.1 mV and reproducibility of ± 0.15 mV), and an automatic Metrohm 800 Dosino burette capable of delivering volume additions down to 1 µL with a reproducibility of ± 0.2 µL. Additionally, measurement cells with a capacity of 25 mL were used and maintained at a constant temperature of T = 298.15 ± 0.1 K through water circulation. The potentiometric cells feature a double wall design to allow for temperature control of the titration solution by circulating water. The analysed solutions were deaerated to eliminate any traces of CO_2 by bubbling them with purified nitrogen saturated with water.

The potentiometric system was interfaced with a PC controlled by the TIAMO 2.5 program, which enables automatic acquisition of pairs of values in ml/mV. This program also controls the entire potentiometric system by regulating the additions of the titrant reagent and recording potential values for each addition. The parameters entered into the program's input define the characteristics of potentiometric data acquisition. These parameters include the maximum time interval between successive readings, the maximum number of reading cycles, the maximum number of data points, the maximum and minimum titrant additions in ml, burette volume, maximum potential threshold, and potential limit for the measurement. Further information are provided in the 1.5.1 section.

10.2 Attenuated total reflectance (ATR)

Attenuated Total Reflectance (ATR) is an analytical method that allows obtaining information about the structure and composition of a sample using the penetration of light. This technique offers significant advantages, including:

- **Direct analysis of liquid and solid samples**: ATR enables the analysis of samples without the need for complex pretreatments, simplifying and speeding up the analysis process.
- **Independence from sample thickness**: The measurement is independent of the sample thickness because it relies on internal reflection, and the path length for a given sample depends on how deeply the infrared energy can penetrate it.

This technique was primarily used for the analysis of polymers and films, but about 25 years ago, the Diamond ATR DiComp[51] was invented, which expanded the use of ATR to many new applications, including the monitoring of chemical reactions.

An attenuated total reflection accessory functions by quantifying the changes that happen to an internally-reflected infrared beam, once it comes into contact with the chosen sample. To do this, an infrared beam is focused onto a crystal. This crystal must have the follow characteristics:

1. **Optically transparent at the energy frequency**: It should be optically transparent at the energy frequency so that the sensor material does not absorb the radiation or absorbs very little.
2. **Higher refractive index than the surrounding medium**: The material of the ATR sensor must have a higher refractive index than that of the surrounding medium so that the ATR device acts as a waveguide, internally reflecting the light energy.

The resulting internal reflections create a transient wave that reaches beyond the outer surface of the optically dense crystal, and then into the sample which is held in contact with it. This initial wave only protrudes by a couple of microns (between 0.5 µ and 5 µ) beyond the surface of the crystal, and into the sample itself. In the parts of the spectrum where the sample absorbs energy, the wave will be either altered or attenuated. The final attenuated energy from each wave is guided back to the original infrared beam, which subsequently leaves via the other side of the crystal and is passed into the spectrometer's detector. The system then uses this data to generate an infrared spectrum.

Depending on the selected optical material and the manufacturing methods of the sensor, the number of reflections or nodes can be precisely controlled. The actual path length for an ATR sensor is determined by the number of internal reflections multiplied by the depth of penetration of the evanescent wave (Figure 34). At each node, a stationary energy wave is emitted at the surface.

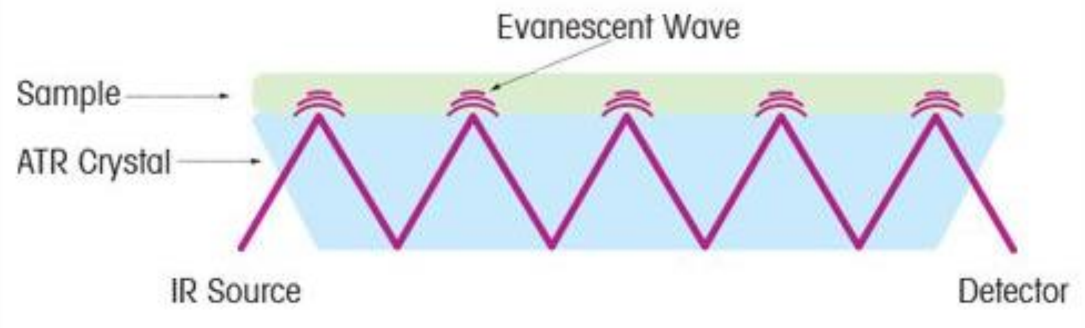


Figure 34: Technical scheme of ATR

This energy is evanescent, meaning its intensity decreases as a function of distance from the sensor's surface. Any substance in direct contact with the sensor is thus exposed to (and analysed by) this energy.

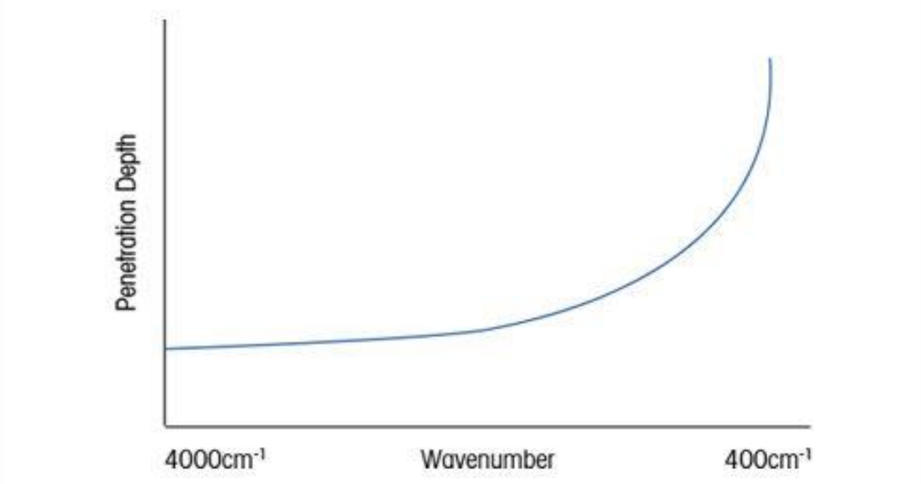


Figure 35: Wavelength trend as a function of the depth of penetration of the ray.

The penetration depth also depends on the specific wavelength of the energy in question (Figure 35). Therefore, when examining a sample with modulated radiation to obtain its spectrum, the position of the peaks will be similar to what is obtained in a transmission/absorbance spectrum, but the intensity of the individual bands will be different from that in the transmission/absorbance spectrum.

The intensity of the spectrum obtained through ATR-IR fundamentally depends on the number of reflections, the depth of penetration of the evanescent wave into the sample, the number of molecules of interest present in the sample, and their respective absorbance.

ATR-IR measurements were performed using a Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer on solid samples that had been previously dried in an oven at 373.15 K to remove moisture.

10.3 Scanning electron microscopy coupled to dispersive X-ray spectroscopy

Scanning Electron Microscopy (SEM) is a powerful imaging technique capable of magnifying a specific region of a sample using a focused high-energy electron beam. Here's how it works in brief:

1. Sample Preparation: The sample to be analyzed is prepared and placed in a SEM chamber, usually under vacuum to avoid electron interactions with airborne particles.
2. Electron Irradiation: A highly focused electron beam strikes the sample. This bombardment causes the release of secondary electrons from the sample's surface.

3. Detectors: Secondary electrons and other types of signals generated by the electron-material interaction are detected by various types of detectors, including the Secondary Electron Detector (SED) and the Backscattered Electron Detector (BSE). These signals are used to create an image based on the surface topography.
4. Energy Dispersive X-ray Spectroscopy (EDS or EDX): Additionally, the sample region can be analyzed to identify the specific elements composing the sample using Energy Dispersive X-ray Spectroscopy (EDS or EDX). When electrons strike the sample, X-rays are emitted with a unique energy signature for the elements present in the sample. These X-rays are detected by the EDS detector to provide information about the chemical composition of the sample.

The combination of SEM and EDS is called SEM-EDX and is extremely useful because it provides a sharp image of microscopic surface structures of a sample and offers details about its elemental composition.

This technique is widely used in a broad range of applications, from basic scientific research to industrial quality control, as it allows for detailed information about the morphology and composition of samples.

Below there is a brief discussion of the general principles of this technique. The interaction between electron and matter generates different types of signals that carry different information about the sample (Figure 36).

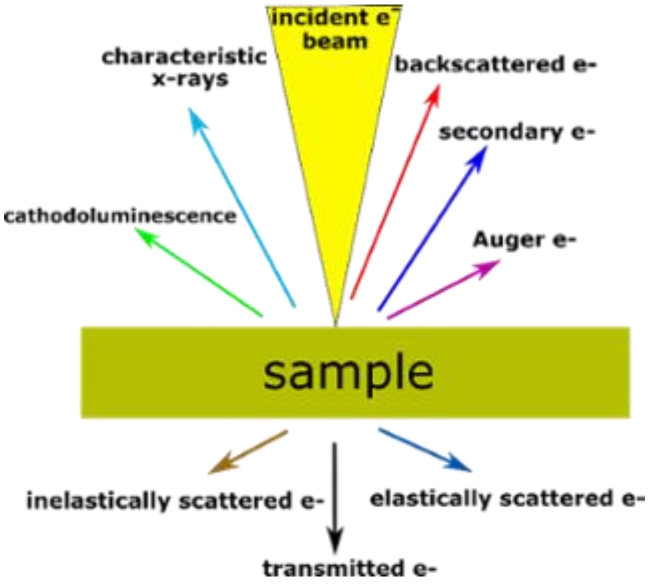


Figure 36: Illustration of the electron-matter interaction and the various signals generated

For example, backscattered electrons produce images with contrast that contains information about differences in atomic number; secondary electrons provide topographical information; cathodoluminescence can provide insights into the electron structure and chemical composition; transmitted electrons describe the intrinsic structure of the sample and its crystallography. Finally, another widely utilized signal type in SEM is X-rays.

Each atom has a unique number of electrons that are typically found in specific positions, as shown in Figure 37. These positions belong to different energy levels.

The generation of X-rays in SEM is a two-stage process. In the first stage, the electron beam strikes the sample and transfers some of its energy to the sample's atoms. This energy can be used by the atoms' electrons to "jump" to a higher energy level or to "jump out" of the atom. If this transition occurs, the electron leaves behind a hole. These holes have a positive charge and, in the second stage of the process, they attract negatively charged electrons from higher energy levels. When an electron fills the hole at a lower energy level, the energy difference of the transition can be released in the form of X-rays.

X-rays have an energy represented by the difference in energy between these two levels. This energy depends on the atomic number, which is a unique property of each element. In this way, X-rays serve as a "fingerprint" of each element and can be used to identify the different types of elements present in a sample.

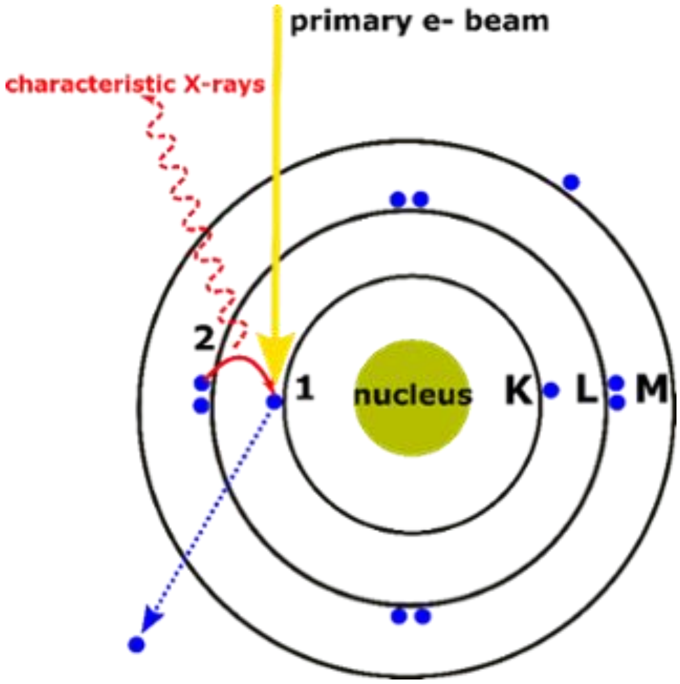


Figure 37: The process of formation of X-rays 1) The energy due to the ejection of the electron leaves behind a hole 2) Its position is filled by another electron from a higher energy level and the ray- X is generated.

These X-rays are detected by specific detectors called silicon drift detectors (SDDs), positioned at a particular angle very close to the sample. SDDs have the capability to measure the energy of incoming photons from X-rays. The larger the solid angle between the detector and the sample, the higher the probability of X-ray detection, and consequently, the better the results obtained.

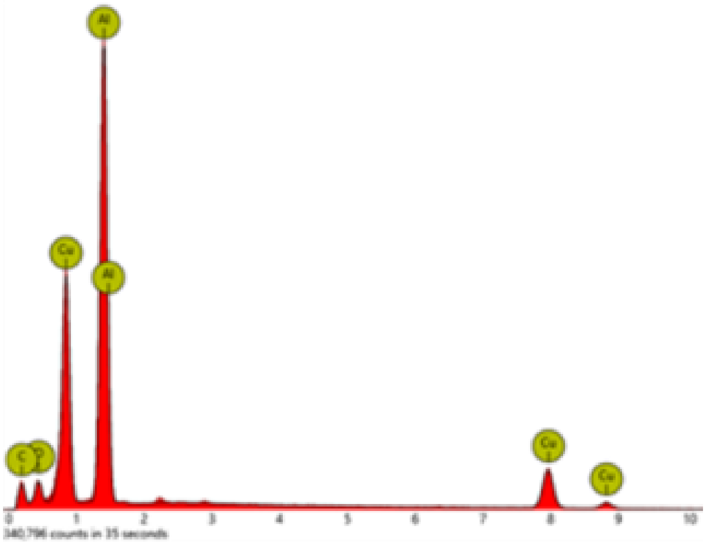


Figure 38: Typical EDX spectrum: the y-axis represents the number of counts and the x-axis represents the X-ray energy. The location of the peaks allows identification of elements, and the height of the peak allows quantification of the concentration of each element in the sample.

The data obtained from EDX analysis consists of spectra with peaks corresponding to all the different elements present in the sample (Figure 38). Each element has characteristic peaks with unique energy levels, which can be found in reference materials.

Furthermore, EDX can be used for both qualitative analysis (identifying the types of elements) and quantitative analysis (determining the percentage concentration of each element in the sample). In most SEM instruments, dedicated software allows for peak identification and the calculation of the atomic percentage of each detected element. Another advantage of the EDX technique is that it is non-destructive and requires little or no sample preparation.

EDX analysis has become a common and valuable technique, so much so that it has become an essential part of SEM. This capability allows SEM images to provide information about the composition of the sample in a straightforward experiment.

10.4 Voltametric measurements

Voltammetry is a class of electroanalytical methods capable of providing qualitative, quantitative, and mechanistic information about electroactive species in the working solution and at the electrode surface. It is based on the measurement in a three-electrode cell of the current (proportional to the rate of the electron transfer process) between the working electrode (W) and the counter electrode (C) as a function of the potential (proportional to energy) between the working electrode (W) and the reference electrode (R), modulated over time. During the measurement, the potentiostat varies the cell voltage (E_c) and detects the current flowing between W and C (I_c) as a function of the potential of the working electrode (E_W), measured by the reference electrode R. What is obtained is a graph where $I_c = f(E_W)$, which is called a voltammogram.

Different voltammetric techniques differ from each other in terms of:

- Working electrodes (material, shape, size, stationary or moving)
- Scanning rate of the potential (slow or fast)
- Shape of the E(t) function

Differential Pulse Voltammetry (DPV) is a voltammetric technique in which a series of fixed-height pulses are overlaid on a potential ramp. The current is recorded just before the pulse and shortly before the end of the pulse, and then the difference between these two current values (I_2 - I_1) is plotted against the applied potential (E).

Differential Pulse Voltammetric measurements were conducted using the Metrohm 663VA Stand-Series 05 system from Metrohm, which includes an mAutolab type III potentiostat (Eco Chemie) with an IME663 interface (Eco Chemie) for managing the working electrode. The entire voltammetric system is operated using GPES software version 4.9 (Eco Chemie).

The voltammetric cell consists of: i) The working electrode: A multimode mercury electrode (MME), model 6.1246.020, operating in static mercury drop mode (SMDE - Static Mercury Drop Electrode) ii) The auxiliary electrode iii) The reference electrode: an Ag/AgCl/KCl (3.0 mol dm^{-3}) reference electrode (model 6.0728.000 + 6.1245.000).

The solutions subjected to voltammetric analysis were deaerated by bubbling purified N_2 gas into the solution, which was also stirred for 600 seconds. A deposition potential of -1.2 volts was applied to the solution for a duration of 1200 seconds. After this period, the solutions were allowed to rest for 10 seconds. At this point, a potential scan was performed from -1.2 to 0.2 volts, with a potential scan rate of 5 mV s^-1 and an amplitude of 50 mV.

Further details are provided in the following section 10.5.2.

10.5 Methods parameters

10.5.1 Potentiometric titration

Potentiometric titrations were performed at T=298.15 K and an initial volume of 25ml using a thermostated cell. The solutions contained 0.15 mol dm^{-3} NaCl, diluted landfill leachate at different dilution and a known quantity of 0.1 mol dm^{-3} hydrochloric acid necessary to acidify the solution and bring it to a pH ≈ 2. A 0.1 mol dm^{-3} sodium hydroxide solution was used as titrant and was set 15µl as minimal addition and 30µl as max. The signal drift was 0.5 mV/min and the waiting time between each addiction was set from a minimum of 30s to a maximum of 60s.

10.5.2 Voltametric measurements

The analyses were conducted using two different procedures:

- For solutions containing the mixture of metals (Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}) prepared at concentrations ranging from 10^{-6} to 10^{-7} mol dm^{-3} and in the presence of an electrolyte ($NaNO_{3(aq)}$ at I = 0.15 mol dm^{-3}), various increasing aliquots of diluted leachate (1:25) were added.
- For solutions containing diluted leachate (1:25) and the electrolyte ($NaNO_{3(aq)}$ at I = 0.15 mol dm^{-3}), increasing aliquots of standard solutions of the metal mixture (Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}) were added.

All parameters used to perform voltametric measurements are collected in Table 14.

Table 14: Voltametric measurements parameters

Metals	**Cd^{2+}**	**Cu^{2+}**	**Pb^{2+}**	**Zn^{2+}**	**Mix metals**
Parameter					
Purge time	100s	300s	300s	300s	600s
Stirrer	off	off	off	off	off
Deposition potential	-0.75 V	-0.2 V	-0.8 V	-1.2 V	-1.2 V
Deposition time	60 s	60 s	70 s	45 s	1200 s
Equilibration time	10 s	10 s	10 s	12 s	10 s
Modulation time	0.01 s	0.05 s	0.05 s	0.05 s	0.01 s
Interval time	0.5 s	0.5 s	0.5 s	0.1 s	0.5 s
Range potential	-0.75 to -0.4 V	-0.2 to 0.15 V	-0.8 to -0.1 V	-1.2 to -0.8 V	-1.2 to 0.2 V
Step potential	5 mV/s	5 mV/s	2.5 mV/s	2.5 mV/s	5 mV/s

10.6 Calculation programs

○ STACO [52] and BSTAC [53]: These programs utilize the nonlinear least squares method to refine protonation and complex formation constants based on potentiometric measurements conducted at different ionic strengths. They also refine the analytical parameters of titrations.

- ES4ECI [54]: This program calculates the equilibrium concentrations of multicomponent systems and simulates titration curves.
- LIANA[55] : LIANA is a program written in the Pascal language with the following features: i) It allows the refinement of parameters in linear and nonlinear equations; ii) The main equation written by the operator in a language similar to BASIC can be broken down into partial equations; iii) Different equations with some common parameters can be considered simultaneously; iv) Different weights can be assigned to experimental variables; v) It can solve functions and optimize them simultaneously.

10.6.1 Programs description

-STACO the sum of the mean square errors in the titrant volume is minimized:

$$U = \sum w(v_{sp} - v_{calc}) \tag{10.2}$$

The program refines the formation constants (β), ionic strength parameters (c_0, c_1, d_0, d_1), Debye-Hückel equation parameters (C and D), initial concentration in the reaction cell (C^0), standard potential (E^0), linear coefficient of the junction potential (j_a), and slope (S_L). The weights at each point on the titration curve are determined by:

$$w = 1/s^2 \qquad s^2 = s_v^2 + \left(\frac{\partial v}{\partial E}\right)^2 s_E^2 \tag{10.3}$$

In some cases, it is convenient to assign unit weights to each point. An additional possibility in STACO involves the following procedure:

I) Parameter refinement (log β, E^0, etc.) using w = 1.

II) A second refinement procedure using $w = 1/\delta^{\varepsilon}$, where $\delta = |v_{sp} - v_{calc}|$, and ε is an empirical factor (ε = 0.5 is a good value in many cases).

Although this procedure lacks theoretical basis, it has been tested for various systems and has proven to be quite useful in some cases. For example, if some points are affected by abnormal errors, the above-mentioned procedure allows them to be disregarded in the second refinement cycle.

- BSTAC program uses the same algorithm as STACO but minimizes potentials instead of volumes.

- **ES4ECI**, considering a system containing N components and M species, the mass balance equations are as follows:

$$C_k = c_k + \sum_i p_{ik}\beta_i \prod_j c_j^{p_i} \tag{10.4}$$

$$C_k = c_k + \sum_i p_{ik}x_i \tag{10.5}$$

Where C_K and c_K are, respectively, the analytical and free concentration of the k-th component, x_i and β_i are, respectively, the concentration and formation constant of the i-th species, p_{ik} (or p_{ij}) is the stoichiometric coefficient of the k-th component in the i-th species, and the indices are defined as k = 1...N, i = 1...M, and j = 1...N. If C_k, p_{ik}, and β_j are known, equation (5.4) represents a series of N nonlinear equations that can be solved simultaneously to find N_{Ck} values.

The problem is then to solve the series of equations:

$$f_k(c) = c_k + \sum_i p_{ik}\beta_i \prod_j c_j^{p_{ij}} - C_k = 0 \tag{10.6}$$

only if $c_K > 0$.

The Newton-Raphson technique allows the values of c_K to be calculated through an iterative procedure. However, since this method can diverge when solving nonlinear equations like (10.4), a damping factor R is used in the iterations:

$$R_k^{(n)} = C_k / C_{k,calc}^{(n)} \tag{10.7}$$

where n is the iteration index. If $R_k^{(n)}$ for the k-th component falls outside the range $\rho^{-1} < R_k^{(n)} < \rho$ (where ρ is a limit chosen within the range 1 < ρ < 10), then the free concentration of the k-th component is damped by the equation:

$$c_{k,smorzato}^{(n)} = c_k^{(n)} (R_k^q)^{(n)} \tag{10.8}$$

where $q = |p_{ik}|_{max}^{-1}$ (for example, q is the reciprocal of the highest stoichiometric coefficient of species containing the k-th component). This procedure is applied to the component for which $\ln|R_k|$ takes the maximum value and is repeated until R_k for all components satisfies the condition $\rho^{-1} < R_k^{(n)} < \rho$. Then, a new cycle of Newton-Raphson iteration is performed.

For solving the system of equation (5.6), the compact Gauss method (modified Gaussian elimination method, easily programmable on a computer) has been chosen. There are several computer programs related to the calculation of equilibrium concentrations, ES4EC (Equilibria in Solution, problem 4, Equilibrium Concentrations), available in different programming languages with various features. For example, ES4ECI, written in Fortran, works with systems containing 20 components and 80 species of each type in a homogeneous phase. It can simulate titration curves, calculate a series of points for distribution diagrams, and compute errors in the free concentrations of components and species.

-**LIANA** (LInear And Nonlinear Analysis) is a program for fitting and optimizing experimental data, written in Pascal. It possesses the following features:

a) It can be used for calculating parameters that require linear and nonlinear equations.
b) Equations are written in a simple manner.
c) The main equation, written by the operator in a language similar to BASIC, can be divided into multiple partial equations.
d) Different equations with common parameters can be considered simultaneously.
e) Different weights can be assigned to each experimental variable.
f) Graphical solutions are provided for immediate data visualization.
g) It can handle multiple different tasks simultaneously, such as solving equations while optimizing functions.

10.7 Reagents

The hydrochloric acid (HCl) and sodium hydroxide (sodium hydroxide, NaOH) solutions were prepared by dilution from their respective concentrated Fluka vials and standardized with sodium carbonate and potassium hydrogen phthalate, which were pre-dried in an oven at T = 383.15 K. The sodium hydroxide solution was stored in dark bottles and protected from atmospheric CO_2 with soda lime traps. The sodium chloride and sodium nitrate solutions were prepared by weighing the corresponding Fluka analytical grade products after drying. The solution of $ZnCl_2$, $CuCl_2$, and $CdCl_2 \cdot 2H_2O$ was prepared by weighing Fluka® puriss. products and standardized with standard EDTA solutions (Fluka).

The potentiometric titrations were performed on solutions containing 0.15 mol dm^{-3} NaCl (Sigma-Aldrich, purity 99%), diluted landfill leachate at 1:5 and 1:25 dilutions, and a known quantity of 0.1 mol dm^{-3} hydrochloric acid (Merck) necessary to acidify the solution and bring it to a pH ≈ 2.

For the voltammetric titrations were used Panreac standard solution for Lead, Copper and Zinc (Copper standard solution Cu=1,000±0,002 g/l, Lead standard solution Pb=1,000±0,002 g/l, Zinc standard solution Zn=1,000±0,002 g/l) and Sigma-Aldrich standard solution for the cadmium (Cadmium standard solution Cd=1000±4 mg/l). In the case of standard metal solutions, they were prepared by dilution at known concentrations, starting from a concentrated multicomponent solution.

10.8 Simplified model – Polyprotic Like Model

Studying solutions composed of polyelectrolytes or a mixture of polyelectrolytes can be complex due to the high number of functional groups with different acid-base properties and complexing capabilities towards metals. Mathematical models are a valuable tool for determining the behaviour of polyelectrolytes in aqueous solutions and have been used to determine thermodynamic parameters, owing the impossibility to experimentally determine the protonation constant of all the functional groups that the polyelectrolyte contains and to their variation when pH change.

It is necessary to consider the dependence of the constants *K* on the degree of dissociation of the polyelectrolyte, where α is:

$$\alpha = [L]/([HL] + [L]) = [L]/[L]_T \qquad (10.9)$$

Indeed, as alpha (α) increases, the charge of the polyelectrolyte increases, leading to an increase in the value of *K.* It is also necessary to consider that the qualitative effect of charge of the polyelectrolyte on protonation constant is given by:

$$\log K = const - \Delta G_E/(RT \ln 10) \qquad (10.10)$$

where ΔG_E is the Gibbs energy charge for removing the proton against the electric field of polyelectrolyte surface.

It is possible to correlate these dependences with the use of two different equations:

1. The modified Henderson-Hasselbalch[56] [57]equation

$$\mathrm{Log}\, K = \log K_n - (n-1)\log[(1-\alpha)/\alpha \qquad (10.11)$$

where n is and empiric parameter and K_n is the protonation constant at half-neutralization.

2. The three-parameter equation based on zeroth approximation proposed by Högfeldt[58]

$$\log K = \alpha^2 \log K_1 + (1-\alpha)^2 \log K_0 + 2\alpha(1-\alpha) \log K_m \qquad (10.12)$$

where K_1 and K_0 are the protonation constants at $\alpha = 1$ and $\alpha = 0$, respectively, while K_m is an intermediate value that takes into account the non-linearity of the log*K* vs. α function. Both equations indicate that log*K* is not constant protonation parameter, but it has been observed that in the range $0.1 \leq \alpha \leq 0.9$, the variation in the protonation constant is less than 2.5 units. Therefore, a simplified approach was proposed about a decade ago called Polyprotic-like Model[59] [60].

The validity of this model has been confirmed by its applicability to a wide variety of polyelectrolytic substances, both organic and inorganic in nature. This demonstrates that the model can reasonably be applied to all substances for which the excess free energy is due to an increase in the value of the electrostatic potential of interaction at a specific site of the polyelectrolyte, influenced by the nearby charged site. It presents itself as a valid alternative to more complex models.

This approach allows treating a polyelectrolyte, in terms of acid-base and complexation properties, as a simple low-molecular-weight ligand, independent of the degree of dissociation (α), taking into account the minimum number of protonation sites necessary to extensively describe the system. The Polyprotic-Like Model has been applied to various classes of polyelectrolytic ligands with different structures, molecular weights, types of functional groups, and the results have been compared with those obtained using the Henderson-Hasselbalch and Högfeldt models. It was observed that the Polyprotic-Like Model offers a much simpler procedure for calculating stability constants without a significant loss of accuracy.

The use of the simplified model is not meant to replace the Högfeldt and Henderson-Hasselbach models, which continue to be valid for determining the acid-base properties of polyelectrolytes. Instead, it serves as a valid alternative to them, allowing the application of calculation procedures and software for speciation studies used for low-molecular-weight ligands. The validity of the simplified model in such calculations has been previously validated in investigations on other classes of polyelectrolytes [61] [62] [63] [64], which is why the authors exclusively used the Polyprotic-Like Model for their current studies.

11 Results and Discussion

11.1 Leachate characterization

11.1.1 Sampling

The leachate samples subject to the investigations were collected from piezometers in a landfill different from Bortolotto large area, using standard methods as indicated in Legislative Decree 152/2006 [14] and in the APAT CNR IRSA 1030 29/2003 manual [65] . These methods involve dynamic sampling using Low Flow Purging for the collection of groundwater samples from piezometers. The piezometers of interest are located both within the landfill body and outside, as highlighted in Figure 39.

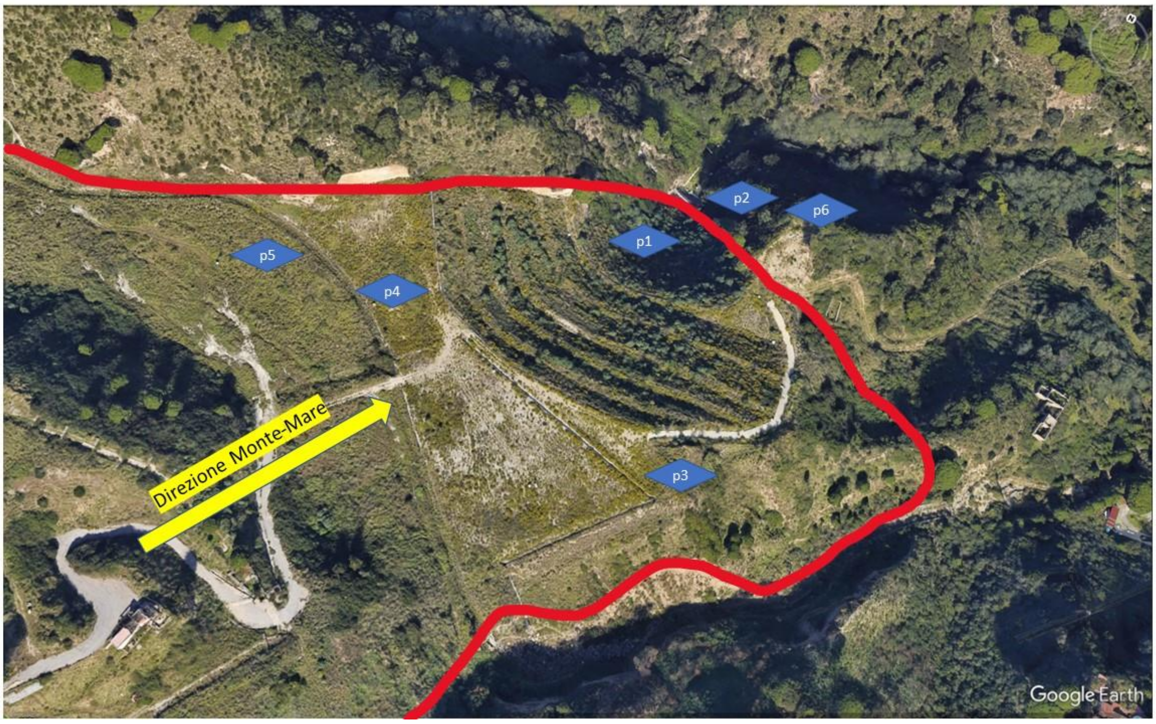


Figure 39: Image of the landfill with the location of the piezometers highlighted and the uphill-seaward direction. The landfill boundary is indicated in red.

To obtain data that would be representative of possible variations during different seasons of the year, two sampling campaigns were carried out, one during the autumn season (November 2021) and another during the summer season (June 2022). The samples collected in both campaigns exhibit a color ranging from dark brown to yellow and all have a distinct pungent odor characteristic of leachate. An example of two samples is shown in Figure 40.

Figure 40: Leachate samples

Field measurements of pH, conductivity, and temperature were conducted using a multiparameter probe, and aliquots of the same sample were placed in various types of containers based on the analytes to be analyzed and treated as reported in the official analytical methods. Portable refrigerators with ice packs inside were used for transportation to preserve samples, and they were subsequently stored in a refrigerator at a temperature of T = 277.15 K until the time of analysis.
or each leachate sample, the analytical package specified in Table 2 of Annex 5, Part IV of Legislative Decree 152/2006, was applied. Official analysis methods were used, as detailed in each test report provided in Appendices 2 and 3.

11.1.2 Determination of organic and inorganic content

In order to determine the percentage of organic and inorganic content, known aliquots (500 ml) of leachate were collected and, after filtration, the samples were dried in an oven at T=373.15 K for 48 hours. A weighed portion of the obtained solid was placed in crucibles, which were then placed in a muffle furnace at T=923.15 K for another 24 hours, ensuring complete volatilization and degradation of the organic fraction. The difference in weight between the initial measurement and the residue weight after 24 hours allowed for the determination of the percentage of organic content and the percentage of inorganic content, which are reported in Table 15.

11.1.3 Comparative physicochemical parameters

The values of the physico-chemical parameters are reported in Table 15 for comparison between the samples collected in November and those collected in June.

Table 15: Physico-chemical parameters of the leachates sampled in November 2021 and June 2022.

Piezometer	**pH**		**Conducibility**		**% Ino**		**% Org**		**Suspended Solids**	
Month sampl.	Nov-21	Jun-22	Nov-21	Jun-22	Nov-21	Jun-22	Nov-21	Jun-22	Nov-21	Jun-22
P1	8,43	7,03	4.88 mS/cm	8.58 mS/cm	81,34	75,86	18,66	24,14	-	34 mg/l
P4	8,2	7,98	2.95 mS/cm	12.89 mS/cm	72,52	76,03	27,48	23,97	-	45 mg/l
P5	8,88	7,8	3.87 mS/cm	14.7 mS/cm	76,7	74,93	23,30	25,07	-	87 mg/l
P6	8,31	7,16	2.71 mS/cm	4.64 mS/cm	78,72	74,95	21,28	25,05	-	27 mg/l
P2	8,4	6,87	1.6 mS/cm	5.02 mS/cm	72,47	74,42	27,53	25,08	-	34 mg/l
P3	8.6	-	3.02 mS/cm	-	68.80	-	19.20	-	-	-

From the table, we can observe, for each sample, percentage values of organic components ranging from approximately 19-28%, against inorganic component values of about 74-76%. The different contribution of rainwater and runoff during different periods of the year does not seem to have significant effects on the percentage composition of the organic/inorganic fraction.

The pH data varies on average between ~8.1 and 8.9, confirming that the leachate is in the methanogenic phase, in accordance with the age of the landfill, which concluded in the 1990s.

Conducibility data, on the other hand, show different values, and some considerations can be made: regarding samples taken within the landfill limits, they present higher conducibility values compared to those taken outside, which is justified by considering the dilution effect of leachate with groundwater.

Elevated conducibility values in less diluted samples depend on the presence of high concentrations of alkali metals, especially Na+, and inorganic anions (such as chlorides, nitrates, and sulfates). Considering the seasonal variability, it is noted that values change significantly based on the sampling season. Different rainfall determines a more acidic pH value for the summer season and a more basic one for the autumn season. In the case of leachates P4 and P5, there are no significant variations, unlike P2 and P6 located outside the landfill, which seem to be significantly affected by the dilution effect due to groundwater intercepting the leachate and mixing with it.

The resulting solution has a composition dependent on the lower quantity of leachate produced during the warmer seasons compared to the winter period and the more soluble inorganic components during this time.

More significant variations are observed, however, for the conductivity parameter, which increases in some cases by 4 times; for example, in the case of the leachate identified as P4, we go from a value of about 2950 μS/cm (Nov. 2021) to 12890 μS/cm (June 2022). This variability in the conductivity parameter can be explained by considering the leachate formation process, i.e., an initial phase of desorption and leaching of soluble components, followed by a dilution effect from excess meteoric or runoff water. Therefore, increased rainfall corresponds to a greater dilution effect and a consequent decrease in the parameter.

Table 16 reports the values of physicochemical parameters for comparison between the samples collected in November and those collected in June.

Table 16: Concentration values of some of the analytes determined from leachate samples.

Leachate	D.Lgs 152/06 Tab2 ann.5, part IV[a]	P4		P5		P1		P6		P2		P3
Parameter\ month sampl.		Nov-21	Jun-22	Nov-21	Jun-22	Nov-21	Jun-22	Nov-21	Jun-22	Nov-21	Jun-22	Nov-21
Aluminium	200 μg/L	13	150	56	270	390	50	62	22		104	1200
Antimony	5 μg/L	1,1	4	2	6	1,4	1	2,4	15		1,3	3
Arsenic	10 μg/L	1,8	15	4	15	40	16	5,8	29		20	6
Cobalt	50 μg/L	3,6	26	6	19	21	17	10	17		17	14
Chromium tot	50 μg/L	16	220	53	290	35	25	18	36		30	29
Iron	200 μg/L	2300	4660	10800	5350	8900	2390	620	3960		3960	26000
Nichel	20 μg/L	6,4	74	11	57	26	22	16	24		24	49
Manganese	50 μg/L	930	320	360	210	2400	2630	830	1580		2140	670
Zinc	3000 μg/L	4,8	42	11	57	37	23	73	60		29	360
Boron	1000 μg/L	580	2800	920	2300	1600	1530	1100	1700		1680	1400
Fluorides	1500 mg/L	250	420	<200	<400	730	1160	420	1000		1140	<200
Sulphates	250 mg/L	350	<2	52	11	23	32	28	15		27	27
Benzene	1 μg/L	0,5	1,5	0,97	1,4	0,2	0,2	0,2	0,7		0,3	0.75
Vinyl Chloride	0,5 μg/L	0,4	2	<0.1	<0.5	<0.1	<0.5	<0.1	<0.5		<0.5	<0.5
1,2-Diciclopropane	0,15 μg/L	<0.1	0,2	<0.1	0,2	<0.1	<0.1	<0.1	<0.1		<0.1	<0.1
Sum of PCB	0,01 μg/L	<0.007	0,06	<0.007	1,9	<0.007	0,004	<0.007	<0.007		0,005	<0.007
Hydrocarbons C>12	-	210	520	220	410	120	150	<40	300		230	300

[a] Concentration values of Contamination Threshold Concentrations (CSC) expressed with respect to Table 2 of Annex 5, Part IV of Legislative Decree 152/2006.

There is a systematic exceedance of the values for Arsenic, Total Chromium, Iron, Nickel, Manganese, and Boron for both the leachate samples within the landfill (P4, P5, and P3) and those located outside the landfill boundaries (P1, P2, and P6).

Furthermore, an increase in analyte concentrations is generally observed in the leachate samples collected in June compared to those collected in November. Therefore, it can be assumed that the contaminant load of the leachate is inversely proportional to the water input, meaning that higher rainfall corresponds to lower concentrations of potential contaminants, even if this consideration is not always observed.

11.2 Solid samples characterization

11.2.1 ATR-IR spectroscopic investigations of the leachate

A few milligrams of solid residue from each leachate sample obtained at T=383.15 K were used for ATR-IR investigations. The spectroscopic analysis was conducted in the range between 400 and 4000 cm^{-1}, using the sample directly without any purification or treatment. The instrument used was a Thermo Scientific iS50 ATR spectrophotometer, and the scans were performed at a resolution of 4 cm^{-1}. The obtained spectra display % transmittance versus wavelength (cm^{-1}).

The objective of these investigations is qualitative in nature, aiming to verify the abundance of different functional groups associated with the dissolved organic component in the leachate. Similar investigations were also conducted on residues obtained after calcination in the muffle furnace at T=923.15 K [66] [67].

Starting from the characterization of samples dried at T=383.15 K, two aliquots were prepared: the first was analyzed as is, while the second was subjected to deionized water washing. The second aliquot was then placed back in the oven at T=383.15 for 24 hours and subsequently dried in a desiccator with silica gel to eliminate any residual traces of moisture to room temperature.

The ATR-IR spectra of the two aliquots, dried and washed, for sample P4 are compared in Figure 41.

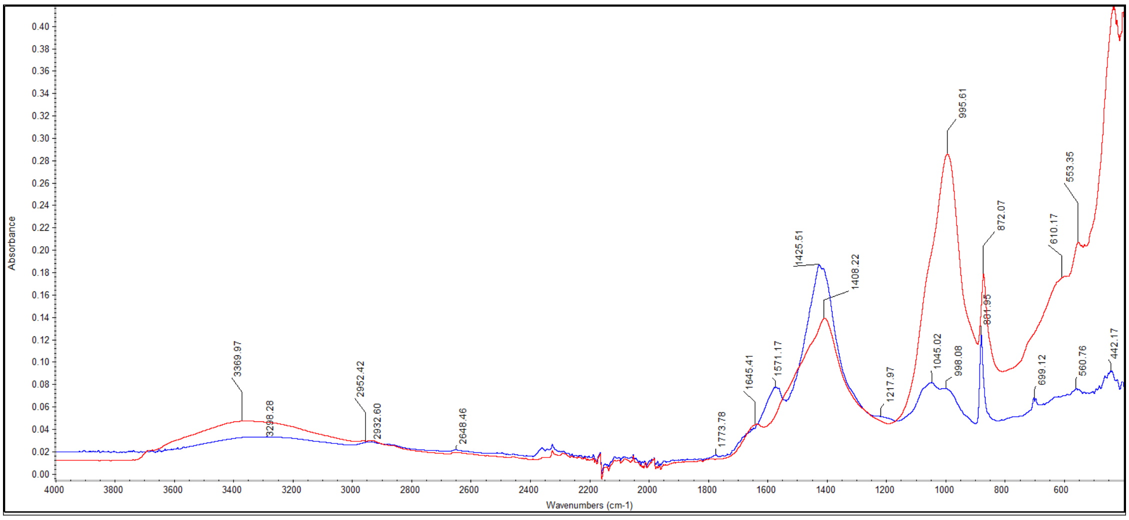


Figure 41: ATR-IR spectrum of leachate sample P4, dried (blue) at T = 383.15 K (analyzed as is) and washed (red).

It can be observed that the washed sample presents much sharper and more defined signals, and in some cases, they are more intense, likely due to the removal of the more soluble inorganic fraction.

In general, characteristic signals of humic acids can be identified in both cases:

- 3400-3300 cm^{-1} stretching of -OH and -NH groups. The low signal intensity is probably due to the dilution of the "aged" leachate.
- 2900 cm^{-1} stretching of -CH groups.
- 1580 cm^{-1} more intense bands, characteristic of aromatic C=C and C=O signals, as well as the carboxylic C=O bond.
- ~1420 cm^{-1} stretching of the C-O and phenolic -OH bonds, and asymmetric stretching of the single C-O bond of the carboxylic group.
- 880 cm^{-1} bending of -OH groups.
- ~1640 cm^{-1} bending of residual hydration water -OH. It disappears in samples calcined at T=923.15 K.
- 1320 cm^{-1} weak band, attributable to the bending of phenolic -OH.
- ~875 cm^{-1} strong band, out-of-plane vibration of the carbonate C-O bond.

There are other bands in the range between 1000 and 1600 cm^{-1}, as well as in the fingerprint region. However, it is difficult to attribute them correctly due to the complexity of the leachate, which is a watery mixture of organic and inorganic compounds. The bands in these regions can result from the absorption of multiple functional groups, as some inorganic hetero-bonds can have significant infrared absorptions.

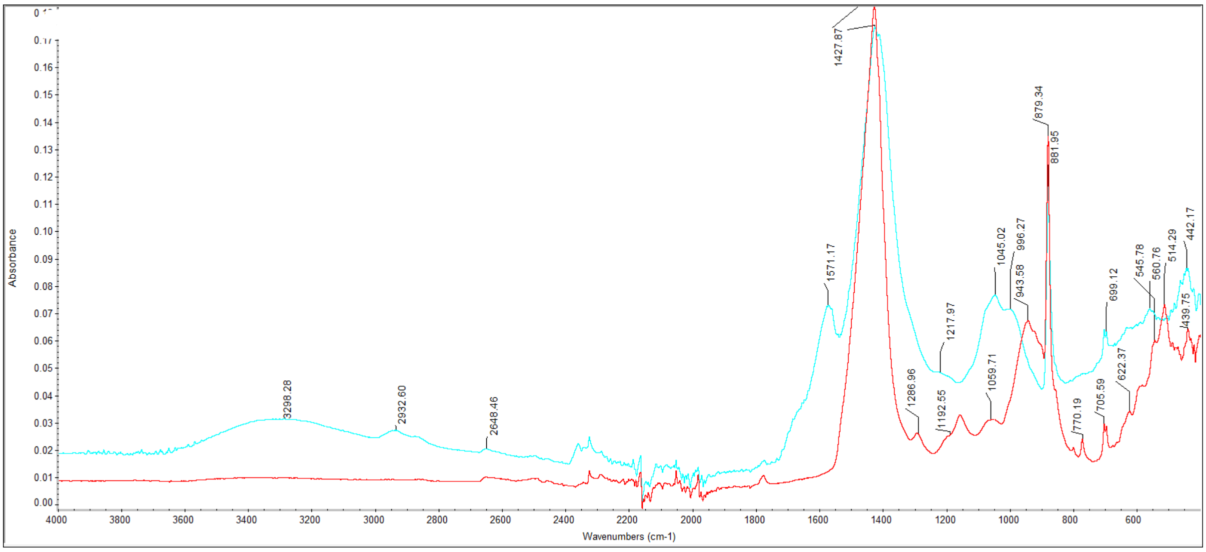


Figure 42: ATR-IR spectrum of leachate sample P4, dried (light blue) at T = 383.15 K, and calcined (red) at T = 923.15 K.

For this reason, part of the residues obtained at T=383.15 K were calcined in a muffle furnace at T=923.15 for 48 hours and, after cooling under vacuum, subjected to analysis. As an example, Figure 42 contains ATR-IR spectra of leachate sample P4, dried (light blue) and calcined (red). From this comparison, several important observations can be made:

- Disappearance of signals related to organic residues in the region above 1550-1600 cm^{-1}.
- Characteristic signals at ~1340 cm^{-1} and 1540 cm^{-1}, likely due to the symmetric and asymmetric stretching of the N=O bond.
- ~1430 cm^{-1} intense signal probably attributable to the S=O bond of the sulfate ion. The presence of this band is also justified by the test reports obtained from the leachate analysis, where sulfate is always present, and in the November 2021 P4 leachate, the concentration of the sulfate anion exceeds the CSC of Legislative Decree 152/2006 [14] .
- ~1100-1200 cm^{-1}, 950 cm^{-1}, and various signals between 500-600 cm^{-1} present in the sample calcined at T=923.15 K can be attributed to the P=O bond [68]. The confirmation of the possible existence of these chemical species in the samples obtained after calcination at T=923.15 K is due to the fact that the complete thermal decomposition of sulfate, nitrate, and phosphate salts occurs at approximately: T > 650°C (SO_4) [69] ; > 600°C (NO_3) [70]; and > 480°C (PO_4) [68] .

However, the complexity of the spectra in the region between 600 and 800 cm^{-1} suggests the presence of signals related to C-X bonds (X = Cl^-, Br^-). Similar investigations were also conducted on the residues at T=383.15 K and T=923.15 K of leachate collected in June 2022. The qualitative results obtained are in complete agreement with those from November 2021 and are consistent with literature data confirming the presence of Dissolved Organic Matter (DOM) in landfill leachate from MSW. The ATR-IR spectra of the other dried and calcined samples are presented in Appendix 4.

11.2.2 SEM-EDX investigations

SEM-EDX investigations were carried out on the leachate residue samples obtained after drying it at T=383.15 K and on the residues obtained after incineration in a muffle furnace at T=923.15 K. The advantage of this spectroscopic technique is that samples can be analyzed without any preliminary treatment. In this case, a few milligrams of each sample were directly subjected to SEM-EDX analysis using a Thermo Fisher Inspect s50 SEM and a Bruker Quantex X Flash 6q/60 EDX.
The P4 and P5 samples, both dried at T=383.15 K and calcined at T=923.15 K, were analyzed. These samples exhibited a higher number of parameters exceeding the CSC of Legislative Decree 152/06.

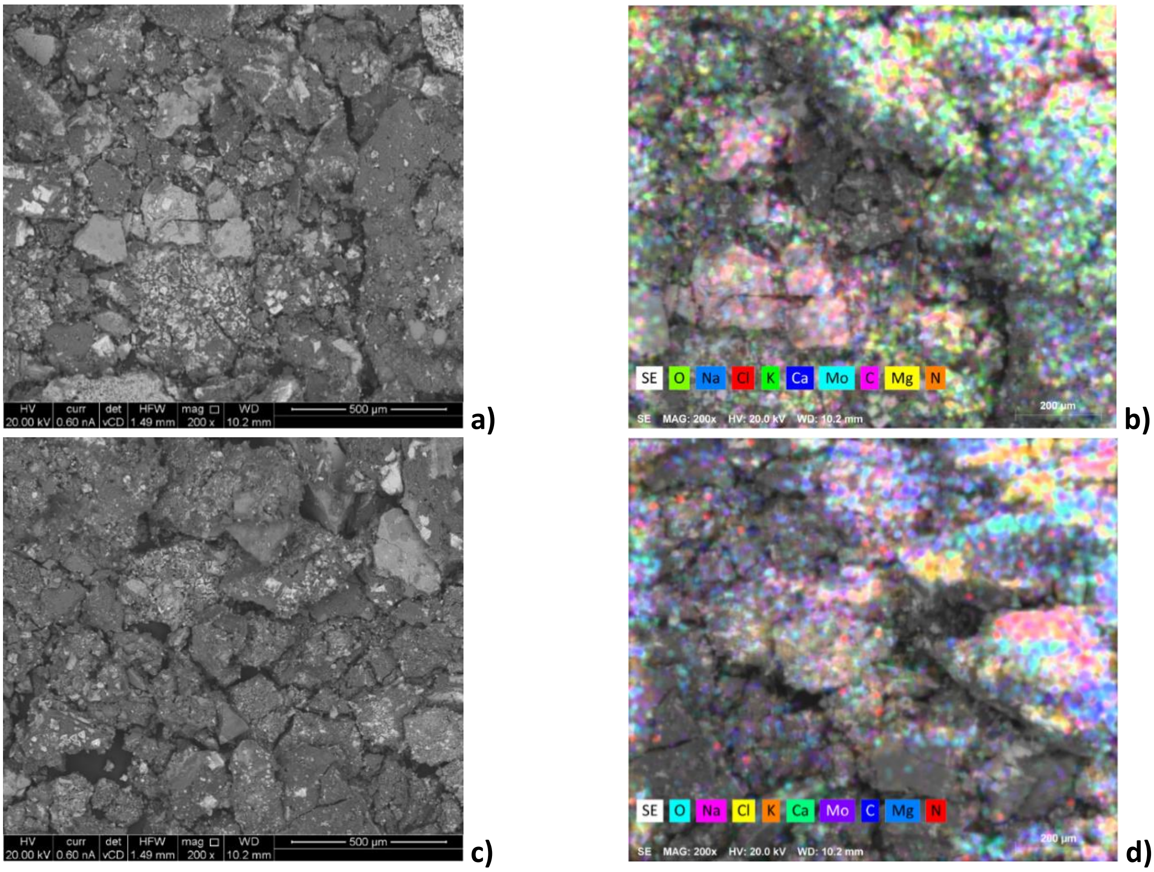


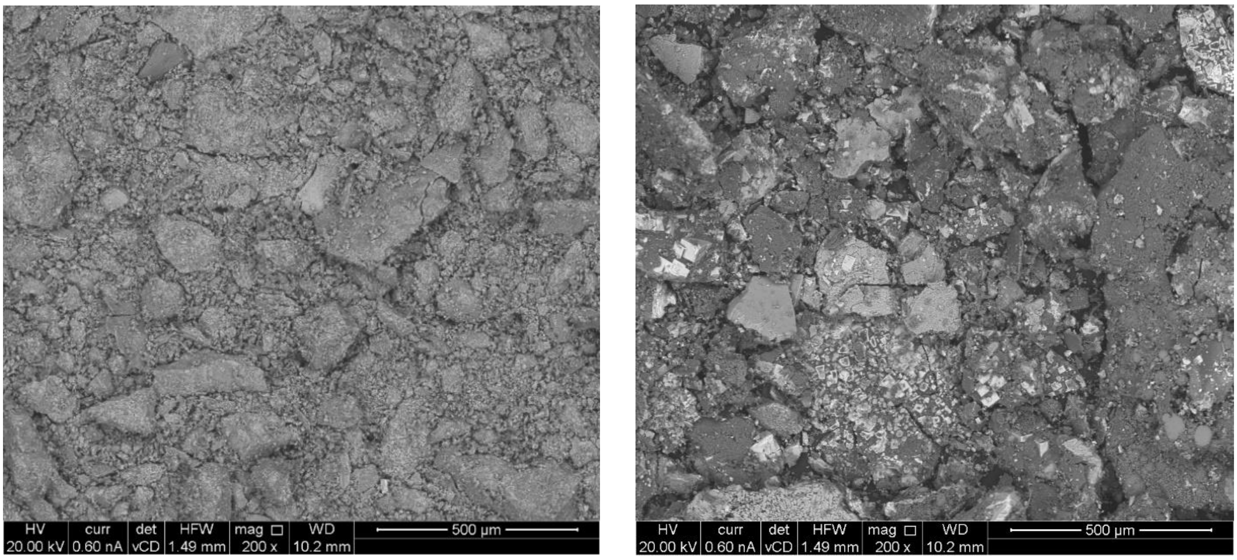
Figure 43: SEM images at 200x magnification of leachate samples P4 (18a, b) and P5 (18c, d) obtained after drying the samples at T = 383.12 K. In images 18b and 18d, each color corresponds to a chemical element.

The morphology of the samples is visible in Figure 43 a-d, and it is evident that both samples have a similar appearance, at least in the analyzed area (200-300 µm) and at the chosen magnification of 200x. However, when comparing the same sample, dried and calcined (Figure 44 a-b), it becomes clear that the loss of the organic fraction contained in the leachate results in only the oxides of the most abundant components remaining.

In Figure 43 b and d, the surface of the sample is visible (b for sample P4 and d for sample P5) with the distribution of the elements highlighted in different colors.

In Figure 45 and 46, to understand the elemental distribution in the leachate samples, the EDX spectra for the dried and calcined P5 sample are shown. The y-axis represents the count number, and the x-axis represents the energy of X-rays. The position of the peaks allows for the identification of elements, and the peak height enables the quantification of the concentration of each element in the sample. From Figure 55, it can be seen that the most abundant elements are C, O, Na, and Cl, as expected. Additionally, Mg and K are present, while the amount of nitrogen is negligible in the analyzed region. This observation is confirmed by FT-IR investigations where no significant bands associated with amine groups of different nature are found. Furthermore, as will be seen later, it is also confirmed by protonation constants determined through potentiometric measurements, which are associated with the -COOH and -OH groups.

The rest of the SEM-EDX spectra obtained for the analyzed samples are presented in Appendix 4.



a) b)

Figure 44: SEM image at 200x magnification of the calcined (a) and dried (b) leachate sample P4.

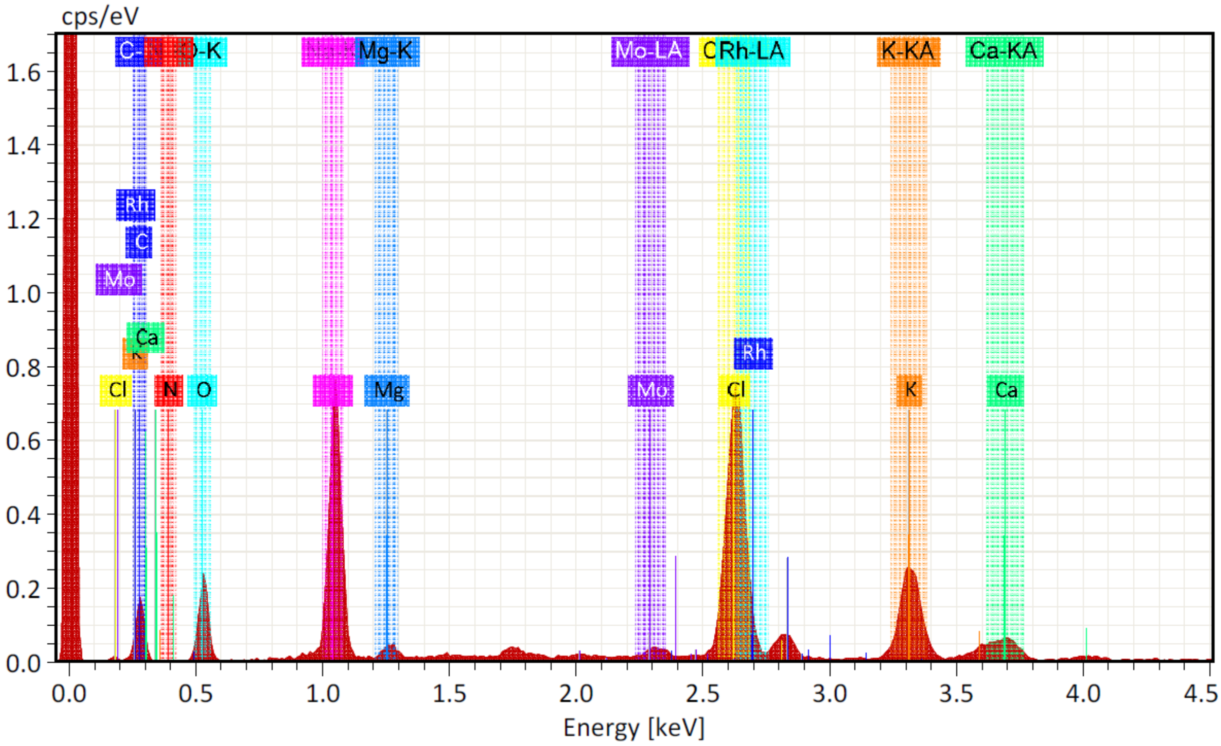


Figure 45: EDX spectrum of the dried leachate sample P5.

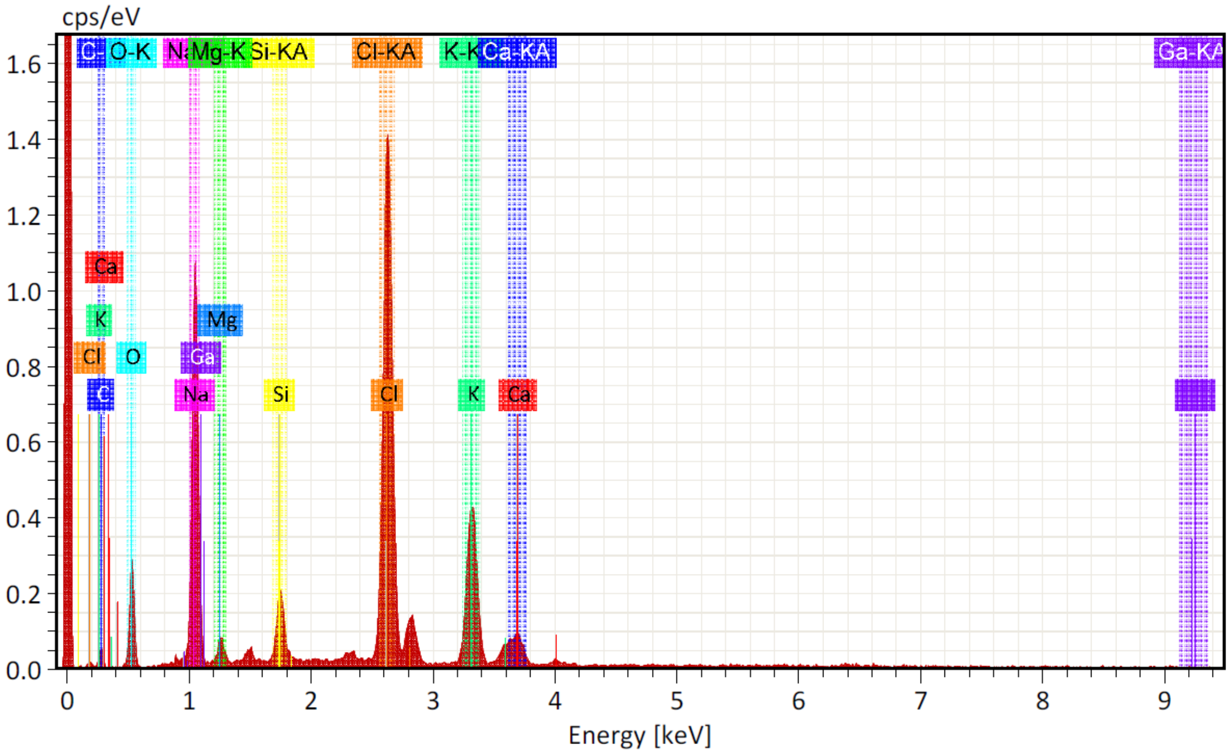


Figura 46: EDX spectrum of the calcinated leachate sample P5.

Table 17 presents the normalized percentage abundances of the main components for each leachate sample (dried and calcined).

Table 17: Percentage abundances of major components in dried and calcined leachate samples.

	Abundances of major components											
	O	Na	Cl	K	Ca	Mo	C	Mg	N	Si	P	Al
P4E[a)]	13.0	15.7	8.55	4.3	1.0	0.2	55.2	0.8	0	0.3	0.2	0
P4C[b)]	22.7	22.9	17.0	8.0	2.2	0.2	17.4	1.5	5.1[c)]	1.4	0.3	0
P5E[a)]	12.9	16.0	8.9	4.4	1.5	0.2	54.5	0.7	0	0.3	0	0
P5C[b)]	28.8	27.1	22.4	9.9	2.2	0	0	1.5	0	2.7	0	0.7

[a)] Dried leachate; [b)] calcinated leachate; [c)] error of 36%

From Table 17, the following observations can be highlighted: i) elements belonging to alkali and alkaline earth metals are the most abundant; ii) chloride is the major inorganic component, while other potential anions such as sulfates (analyzed during characterization, but sulfur was excluded during EDX analysis) and phosphates, if present, are in much lower percentages. For example, in leachate P4, we observe low percentages of phosphorus; iii) for all elements, except carbon, there is an increase in percentages in the calcined sample compared to the dried one; iv) in the calcined samples, the percentage of carbon decreases due to the calcination and elimination of organic substances; v) the carbon still present in the calcined samples is likely due to residues of organic matter refractory to the calcination temperature and/or the presence of inorganic carbon, such as various carbonate salts.

11.3 Study of acid-base properties

For the study of the acid-base properties of the leachates, potentiometric titrations were carried out at a temperature of T=298.15 K, and NaCl was added to achieve the desired ionic strength (I=0.15 mol dm^{-3}). The leachate sample was previously filtered through a 0.45 mm Whatman filter to retain all possible suspended solids, and the filtrate was stored at T = 277.15 K. Titrations, as described in the experimental section, were performed using a [H$^+$] ion-selective electrode. Several measurements were taken for each sample at different leachate:ionic medium solution dilution ratios:

5.25

7:25

10:25

15:25

Since the pH of the sampled leachates is generally alkaline (~7.8-8.6), aliquots of a 0.1 mol dm^{-3} HCl solution were added to adjust the solution pH to around 2.

The titrant (0.1 mol dm^{-3} NaOH solution) was added using a potentiometric system consisting of a Methom 809 potentiometer with a Methom 801 stirrer, an Orion combined glass electrode Ross 8102 (with an experimental resolution of 0.1 mV and reproducibility of ± 0.15 mV), and a Metrohm Dosimat automatic burette capable of making additions in volumes up to 1 µL with a reproducibility of ± 0.2 µL. The system was connected to a PC, and titrations were controlled by the software Metrohm TiAmo 2.5, that, based on the potential gradient and its stability during titration, made predetermined additions of titrant.

Titrations were performed by collecting the couple of data electromotive force (e.m.f./mV) vs. volume of titrant (ml of NaOH) until the pH reached approximately 12.

Each measurement was always preceded by a titration of HCl with standard NaOH under the same experimental conditions to determine the formal electrode potential (E°).

The titration curves exhibit the typical profile of a weak acid titrated with a strong base, but differences were highlighted through the study of different samples.

Taking leachate P1 as an example, as shown in Figure 47, three distinct bands can be distinguished: the first corresponds to the neutralization of the residual strong acid (HCl), significantly lower than the amount of initially added inorganic acid since a significant portion was neutralized by all alkaline species present in the sample, whose initial pH was around 8.5. The second peak, falling in the pH range between 5.5 and 6, can be attributed to carboxylic groups, while the third, in the pH range between 9 and 9.5, to the -OH groups of natural organic matter.

It is noticeable, by observing the graph of the first derivative of the potential (expressed in mV) with respect to the ml of added titrant, that the concentration of -COOH groups in the leachate sample is significantly lower than that of -OH groups.

Leachate P6, on the other hand, shows a different profile, as seen in Figure 48, where the second peak is not distinguishable, absorbed by the peak of the inorganic acid residue. This is consistent with the initial pH difference of the titration, which, with the same added HCl, is 0.6 more acidic than that of sample P1 (P1 initial pH 2.1, P6 initial pH 2.7).

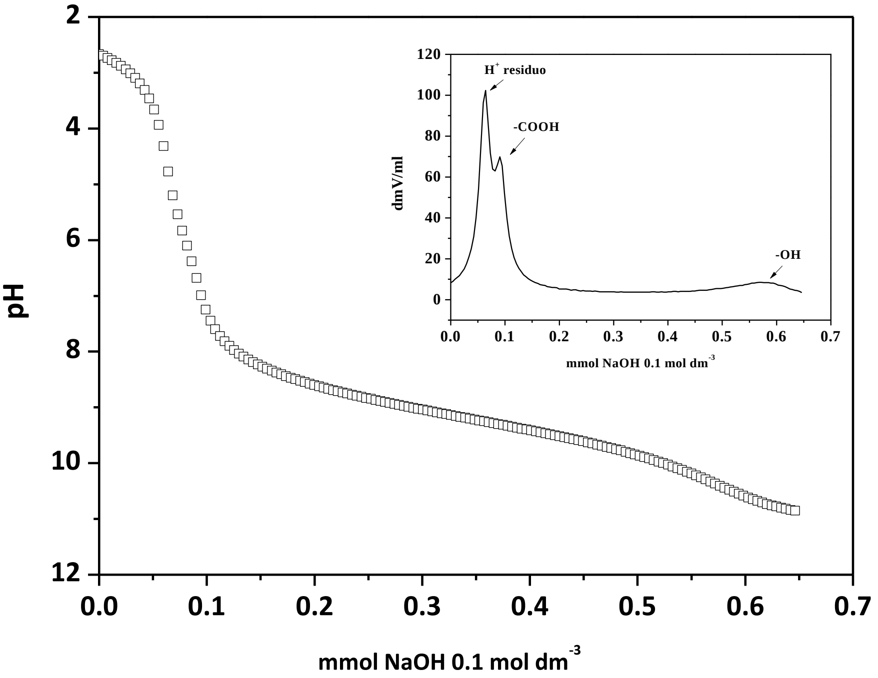


Figure 47: Titrations curve of leachate P1 sampled in June 2022, diluted at a 5:25 ratio with a 0.15 mol dm^{-3} NaCl solution, and titrated with 0.15 mol dm^{-3} NaOH (the inset shows the first derivative of the titration curve).

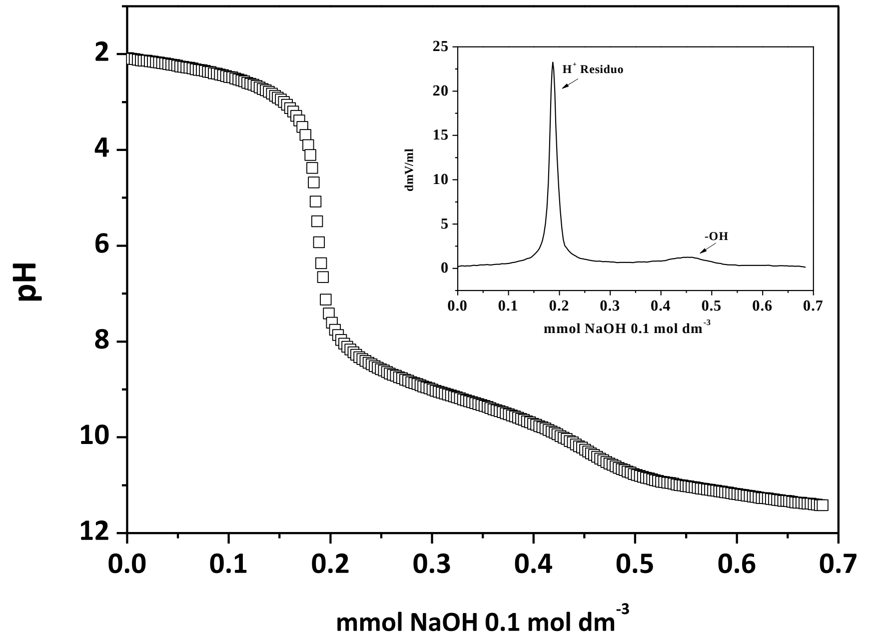


Figure 48: Titrations curve of leachate P6 sampled in June 2022, diluted at a 5:25 ratio with a 0.15 mol dm^{-3} NaCl solution, and titrated with 0.15 mol dm^{-3} NaOH (the inset shows the first derivative of the titration curve).

In general, the different behavior of the various leachates under the same dilution and ionic medium is shown in Figure 49, which depicts the titration curves of the leachates sampled in June 2022.

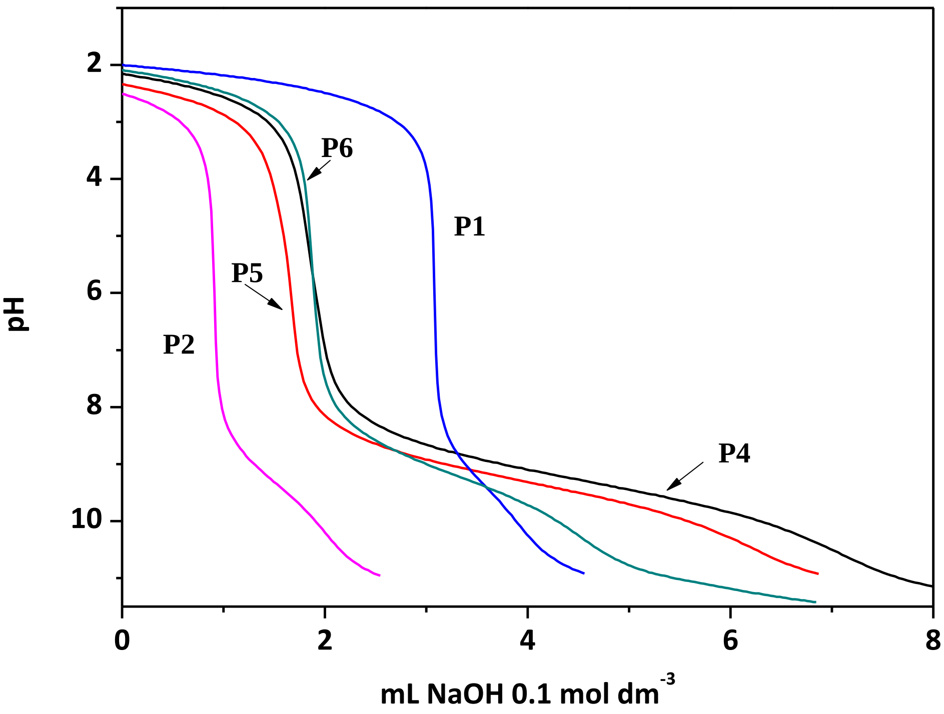


Figure 49: Acid-base titration curves (dilution ratio 5:25 with NaCl 0.15 mol dm^{-3}) of the leachates sampled in June 2022.

Comparing individual titration curves, it is possible to notice slight differences in profiles, with a greater similarity between samples P4 and P5. The amount of titrant needed to reach a pH of about 11 varies for each solution, associated with the different initial pH of the leachates, which, in turn, is linked to the content of alkaline species present in the sample capable of neutralizing the inorganic acid. Finally, for some of the curves (P1, P4, and P5), there is a more pronounced inflection in the alkaline zone. Through the calculation of the first derivative of the titration curve, the quantity (in mol dm^{-3}) of -COOH and -OH groups were determined for each sample, and the results were compiled in Table 18.

Table 18: Concentrations of -COOH and -OH groups determined for each leachate.

Piezometer	COOH[a)]		OH [a)]	
Sampling month	Nov-21	Jun-22	Nov-21	Jun-22
P1	0.0275	0.0003	0.1034	0.0116
P4	0.0102	0.003	0.0252	0.0990
P5	0.0021	0.004	0.0211	0.1059
P6	0.003	0.0009	0.0908	0.0229
P2	-	0.0006	-	0.021
P3	0.0024	-	0.0225	-

a) Concentrations expressed in mol dm^{-3}.

The presence of other functional groups such as amino or thiol groups has not been considered because the percentage of nitrogen and sulfur can be considered negligible, as highlighted by the performed SEM-EDX analyses.

To confirm the calculations obtained from the individual titration curves, the concentration determination of -COOH and -OH groups was also performed using the calcium acetate and barium hydroxide titration method [71], yielding entirely comparable results (not reported because used as simple check/comparison).

Considering the differences between the same sample collected in June and November, some observations can be made:

1. Regardless of the period, the concentration of carboxylic groups is consistently much lower than that of alkaline groups, mainly attributable to -OH groups, in line with literature reports [72].
2. For each leachate/sample contaminated with leachate, different molar ratios and concentrations between [COOH]/[OH] are observed.
3. The amount of HCl required to acidify the same sample collected in the two different periods of the year differs and is higher for samples collected in June. For example, Figure 50 shows the titration curves for leachate P5 sampled in November 2021 and June 2022, diluted in the same 5:25 ratio with a 0.15 mol dm^{-3} NaCl solution and to which quantities of HCl were added until reaching a pH of ~2.
4. These solutions were then titrated with 0.1 mol dm^{-3} NaOH. From Figure 50, we observe that the profiles of the curves are completely different, especially after the neutralization of carboxylic groups. In the case of leachate P5 sampled in June 2022, we can observe that a

significantly higher amount of titrant is needed to neutralize the dissociable groups in an alkaline environment (-OH). This is also confirmed by the results obtained in Table 18. In fact, for leachate P5 sampled in November 2021, the quantity of -OH groups were determined to be 0.0211 mol dm^{-3}, compared to a value of 0.1059 mol dm^{-3} for the analogous leachate sampled in June 2022.

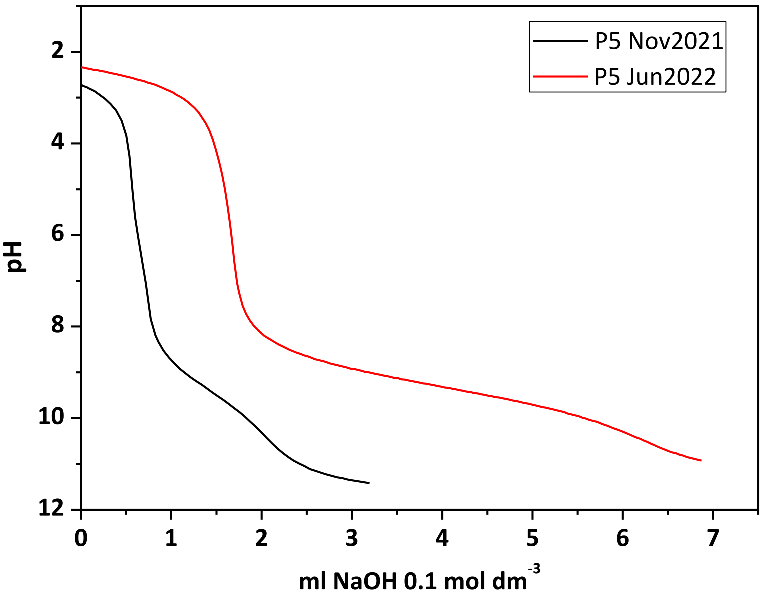


Figure 50: Comparison of the titration curves of leachate P5 sampled in November 2021 and June 2022. Dilution ratio 5:25 ml with 0.15 mol dm^{-3} NaCl.

The knowledge of the analytical concentration of -COOH and -OH groups allowed us to process the data collected by means of the potentiometric titrations to determine the protonation constants of individual leachates. To achieve this, the Polyprotic Like model, described earlier, was employed, which minimizes the number of protonable sites needed to describe the acid-base properties of the samples and the potential variation with pH. This approach enabled the calculation of protonation constants by the minimization of the mean squared differences of the couple of data e.f.m. vs ml of titrant.

Two different models were proposed:

- The first considers the dissolved organic matter consisting of two repeating units. The first unit describes the behavior in an acidic environment and is composed of a functional group resembling a carboxylic group, while the second describes the behavior in a basic environment and is composed of a group resembling alcoholic/phenolic groups.

- The second model is similar to the first, but the first dissociable repeat unit in an acidic environment consists of two groups resembling carboxylic groups, while the second still represents a single unit resembling alcoholic/phenolic groups.

The overall protonation constants (log β) of each repeating unit can be expressed as follows:

$L2 + i\,H^+ = H_iL2$ (i=1-2)

$L1 + H^+ = HL1$

Table 19 summarizes the results for both samples collected in November 2021 and those collected in June 2022

Table 19: Overall protonation constants of leachates sampled in November 2021 and June 2022.

Leachates	November 2021			June 2022		
	$\log\beta(HL2)$	$\log\beta(H_2L2)$	$\log\beta(HL1)$	$\log\beta(HL2)$	$\log\beta(H_2L2)$	$\log\beta(HL1)$
P1	8.40±0.02[a]	13.86±0.03	9.348±0.001	3.56±0.07	6.06±0.20	9.323±0.002
	5.83±0.03		9.293±0.002	2.60±0.03	-	9.302±0.002
P4	4.95±0.03	8.04±0.09	9.273±0.001	7.82±0.02	12.64±0.01	9.334±0.008
	3.47±0.02		9.318±0.001	5.07±0.01	-	9.275±0.001
P5	6.77±0.03	11.05±0.04	9.320±0.001	6.34±0.01	10.40±0.02	9.303±0.001
	5.62±0.03		9.310±0.001	5.52±0.01	-	9.311±0.001
P6	-	-	-	5.81±0.08	9.05±0.10	9.278±0.001
	4.07±0.01		9.329±0.05	5.47±0.04	-	9.337±0.002
P2	-	-	-	-	-	-
	-	-	-	2.70±0.04	-	9.457±0.003
P3	8.87±0.02	14.70±0.03	9.412±0.002	-	-	-
	5.95±0.01		9.348±0.001	-	-	-

[a] 95% of the Confidence Interval (C.I.)

These data are in very good agreement with the protonation constants already determined by our research group for some standard humic and fulvic acid, by using the approach that consider only two protonation steps, one per repeating unit. [60]

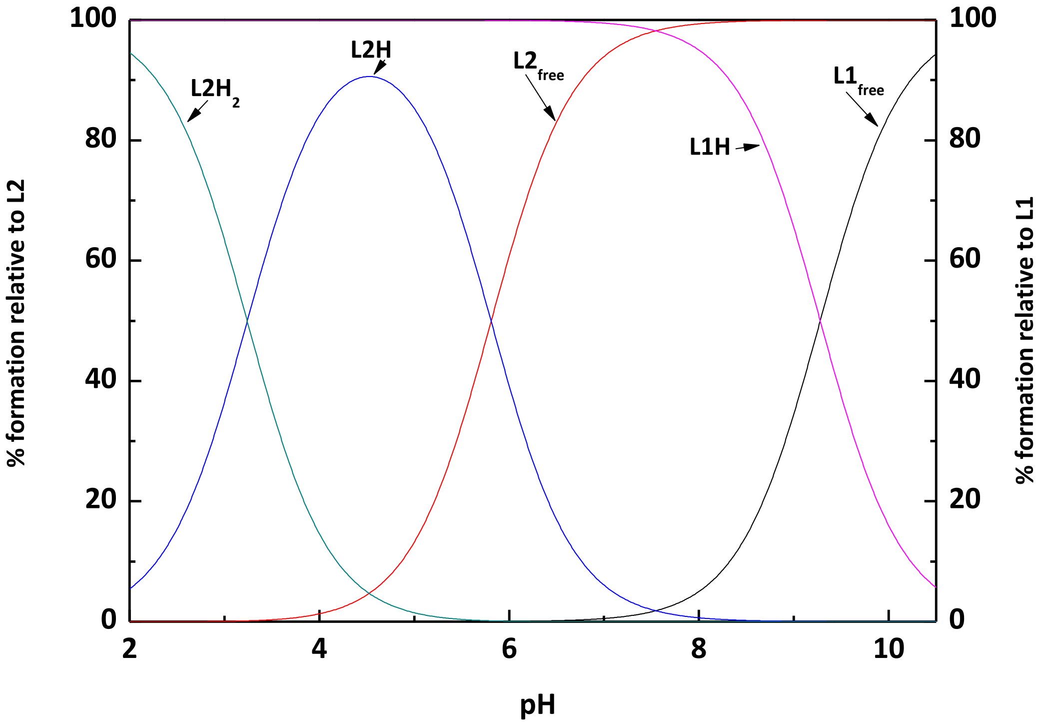


Figura 51: Distribution diagram of protonated species of leachate P4.

Experimental conditions: c_{L1} = 22.9 mmol dm^{-3}; c_{L2} = 0.9 mmol dm^{-3}; C_{Cl-} = 150 mmol dm^{-3}, at T = 298.15 K.

In Figure 51, the distribution diagram of protonated species of leachate P4 is shown. It can be observed that in the pH range below 6.5, only the protonated species involving carboxylic groups are present, with formation percentages for both species linked to ligand L2 exceeding 90%. The only species related to ligand L1, and thus to the -OH group, starts deprotonating around pH 7, becoming free to interact with positively charged species.

Choosing the appropriate model is not straightforward, as leachate is a matrix with high composition variability, depending on both the site and the sampling period chosen, resulting in different concentrations of the main functional groups considered.

One possible criterion for selecting the most suitable speciation model to describe the acid-base properties of leachates could be to consider the concentration of carboxylic groups. In this case, the first model should be used for leachates containing low concentrations of carboxylic groups, and the second model for those containing a higher concentration.

11.4 Metal-leachate interactions

In the context of environmental issues related to the possible presence of organic and inorganic contaminants in various environmental matrices, the simple detection of total concentrations of these contaminants often does not provide a complete understanding. This is because the potential hazard, in terms of toxicity, carcinogenicity, mobility, and transport, depends on the specific chemical form in which these contaminants may be present in a given system. The formation of these specific chemical forms is influenced by various factors, including temperature, pH, and redox potential, in addition to the complexity of the system in which the components are dissolved.

Furthermore, since all natural systems are composed of a variety of components, with the simultaneous presence of numerous different elements interacting with each other in a complex manner, often in relation to their concentrations and molar ratios, assessing the potential hazard of a component becomes a complex challenge that requires a targeted study of speciation. Consequently, to create a comprehensive model of speciation in a fluid, that is, to quantitatively describe the state of different chemical species, it is necessary to consider all possible interactions between ligands and metals dissolved in the fluid, taking into account the influence of trace components.

Despite the increased attention to environmental concerns, pollution, and their effects on living organisms and humans, the importance of understanding the toxicity and bioavailability of metals and ligands in natural systems and their impact on health has also emerged.

This underscores the need for in-depth studies on the behavior of the major classes of ligands and metals present in biological fluids and natural waters. Such studies aim to determine in which chemical forms these substances can become toxic and to identify mechanisms for their removal or inhibition of hazardous effects. To achieve this goal, it is essential to understand a series of parameters that regulate their behavior, including transport, absorption, desorption, precipitation, dissolution, and complexation in natural systems. This knowledge requires a thorough understanding of the chemical behavior of these components in the environment, including all thermodynamic parameters that influence their acid-base properties and complexation capacities. The study of the speciation of a component in a system allows for a proactive assessment of the mechanism of action, providing crucial information that cannot be obtained solely by measuring the analytical concentration of the element itself. This is particularly relevant in complex situations, such as landfill leachate, which contains a wide range of organic and inorganic components, both natural and anthropogenic. In such cases, where the concentrations of these components may vary over time due to the intrinsic characteristics of the leachate, speciation studies play a fundamental role in understanding and managing environmental issues.

For this reason, a significant portion of our studies has been aimed at investigating the interaction of organic matter contained in various leachates with some metals (Cd^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}), assuming the concentration of the given metal already present in the leachate as the "blank" value, known from characterization analyses according to Legislative Decree 152/2006.

The importance of studying metal/leachate species lies not only in understanding the system itself, thus allowing knowledge of the formation constants of the species, their percentage of formation, and their relative distribution with varying pH but also in determining the main species present at different pH levels.

This information can be strategically important for understanding the species present under the sampling conditions, but more importantly, it provides precise information about the potential of each leachate as a carrier of contaminants through soil and/or groundwater.

In this study, considering the long times required for analyses and the complexity of data processing, we chose to investigate only the landfill leachates identified as P4 and P5, focusing on the June 2022 samplings. Once again, the Polyprotic Like Model was used.

Tables 20 and 21 contain the speciation models and corresponding formation constants for each system. It can be observed that, each leachate samples, is featured by different speciation models, i.e. metal/ligand complexes.

Furthermore, even when the stoichiometry of the metal:ligand species is the same, a variation in stability is observed. This phenomenon can be explained by considering the following aspects:

1. The analyzed landfill leachates clearly exhibit different acid-base behaviors, as highlighted by the protonation constants and titration curves shown in Figure 49. These differences are directly related to the different concentrations of -COOH and -OH groups, as indicated in Table 18.
2. It is important to note that in speciation studies in multicomponent systems, the speciation, stability, and distribution of species can be influenced by the presence and concentration of secondary components that may interact with both the metal under study and the ligand. Therefore, during the analysis of potentiometric data (mV vs. ml), a speciation model was chosen based on the significant presence of components in the leachate, such as chloride, sulfate, fluoride, and so on.

In Tables 22 and 23, we provide the speciation model used as input for each metal/leachate system.

Table 20: Formation constants of species for landfill leachates P4 and P5 with Cd^{2+} in NaCl 0.15 mol dm^{-3} at T = 298.15 K

leachate	species				
	log $\beta_{M(L2)OH}$ [a)]	log $\beta_{M(L2)Cl}$	log $\beta_{M2(L2)OH}$	log $\beta_{M2(L2)Cl}$	log β_{ML1}
P4	8.5±0.10 [b)]	14.78±0.09	13.60±0.10	19.20±0.20	4.67±0.01
P5	-	6.65±0.04	4.73±0.02	10.97±0.03	3.61±0.01

[a)] The formation equilibrium refers to the reaction: $p\ M^{2+} + q\ L_2^{2-} + n\ Cl^- + r\ H_2O = M_p(L_2)_{(q)}Cl_nOH_r^{(2\cdot p-(2\cdot q-n-r))} + r\ H^+$; [b)] $M^{2+} + L_1^- = ML_1^+$; [b)] 95% Confidence Interval (C.I.)

Table 21: Formation constants of species for landfill leachates P4 and P5 with Zn^{2+} in NaCl 0.15 mol dm^{-3} at T = 298.15 K

leachate	species				
	log $\beta_{M(L2)}$ [a)]	log $\beta_{M(L2)2}$	log $\beta_{M(L2)H}$	log $\beta_{M2(L1)2}$	log $\beta_{M(L1)2}$
P4	6.69±0.05 [b)]	12.8±0.2	-	-	7.02±0.01
P5	8.70±0.10	-	11.10±0.10	9.90±0.10	-

[a)] The formation equilibrium refers to the reaction: $p\ M^{2+} + q\ L_2^{2-} + r\ H^+ = M_pL_{2(q)}\ H_r^{(2\cdot p+r-(2\cdot q))}$; [b)] $p\ M^{2+} + q\ L_1^- = M_p(L_1)_q^{(2\cdot p-q)}$; [b)] 95% Confidence Interval (C.I.)

The measurements were carried out by adding known quantities of NaCl to work under buffered conditions of ionic strength. It is also necessary to consider the high concentration of chloride ions naturally present in the leachate. For this reason, considering the tendency of the metals under consideration to form stable species with Cl^- (i.e., CdCl and ZnCl), these were included in the speciation model, along with the hydrolytic species of the metal. In the case of Cd^{2+}, the mixed hydrolytic species CdOHCl was also included [73]. Regarding sample P4, the concentration of naturally occurring fluoride ions is not negligible (~1150 mg dm^{-3}). Therefore, in the speciation study, both protonated species of fluoride ions (HF and HF_2) and the CdF species were considered. All these differences inevitably lead to considering each leachate as entirely independent systems from each other, despite being sampled from the same landfill.

Table 22: Speciation model and formation constants of the species reported in the input for the Cd^{2+}/P4 and Cd^{2+}/P5 systems.

P4		P5	
	$\log \beta_{pqr}$ $^{a)}$		
kW	-13.740	kW	-13.740
$(Cd)(OH)$ $^{b)}$	-10.450	$(Cd)(OH)^{b)}$	-10.450
$(Cd)(OH)_2$ $^{b)}$	-20.730	$(Cd)(OH)_2$ $^{b)}$	-20.730
$(Cd)(OH)_3$ $^{b)}$	-33.300	$(Cd)(OH)_3$ $^{b)}$	-33.300
$(Cd)(OH)_4$ $^{b)}$	-46.640	$(Cd)(OH)_4$ $^{b)}$	-46.640
$(Cd)2(OH)$ $^{b)}$	-9.010	$(Cd)_2(OH)$ $^{b)}$	-9.010
$(Cd)_4(OH)_4$ $^{b)}$	-32.070	$(Cd)_4(OH)_4$ $^{b)}$	-32.070
$(Cd)(Cl)$ $^{c)}$	1.510	$(Cd)(Cl)$ $^{c)}$	1.510
$(Cd)(Cl)_2$ $^{c)}$	1.920	$(Cd)(Cl)_2$ $^{c)}$	1.920
$(Cd)(Cl)_3$ $^{c)}$	1.490	$(Cd)(Cl)_3$ $^{c)}$	1.490
$(Cd)(Cl)(OH)$ $^{c)}$	-7.890	$(Cd)(Cl)(OH)$ $^{c)}$	-7.890
$(F)(H)$ $^{d)}$	2.960	-	-
$(F)_2(H)$ $^{d)}$	3.520	-	-
$(Cd)(F)$ $^{b)}$	0.939	-	-
$(L2)(H)$ $^{d)}$	7.820	$(L2)(H)$ $^{d)}$	6.340
$(L2)(H)_2$ $^{d)}$	12.640	$(L2)(H)_2$ $^{d)}$	10.400
$(L1)(H)$ $^{d)}$	9.334	$(L1)(H)$ $^{d)}$	9.303

$^{a)}$ Formation constants valid at I = 0.15 mol dm^{-3} in NaCl and T = 298.15 K; $^{b)}$ $p\ M^{2+} + r\ H_2O = M_p(OH)_r^{(2p-r)} + r\ H^+$ [73]; $^{c)}$ $M^{2+} + i\ L^- + H_2O = ML_i(OH^{)(2-q-1)} + H^+$ ($L = Cl^-$; F^-) [73]; $^{d)}$ $p\ H^+ + L^{n-} = H_pL^{(-n+p)}$ [73]

Table 23: Speciation model and formation constants of the species reported in the input for the Zn^{2+}/P4 and Zn^{2+}/P5 systems.

P4		P5	
	log $\beta_{pqr}$$^{a)}$		
kW	-13.740	kW	-13.740
(Zn)(OH) $^{b)}$	-9.160	(Zn)(OH)	-9.160
(Zn)(OH)$_2$ $^{b)}$	-17.110	(Zn)(OH)$_2$	-17.110
(Zn)(OH)$_3$ $^{b)}$	-28.370	(Zn)(OH)$_3$	-28.370
(Zn)(OH)$_4$ $^{b)}$	-40.630	(Zn)(OH)$_4$	-40.630
(Zn)$_2$(OH) $^{b)}$	-8.920	(Zn)2(OH)	-8.920
(Zn)$_2$(OH)$_6$ $^{b)}$	-57.480	(Zn)$_2$(OH)$_6$	-57.480
(Zn)(Cl) $^{b)}$	0.040	(Zn)(Cl)	0.040
(F)(H) $^{c)}$	2.960	-	-
(F)$_2$(H) $^{c)}$	3.520	-	-
(L2)(H) $^{d)}$	7.820	(L2)(H)	6.340
(L2)(H)$_2$ $^{d)}$	12.640	(L2)(H)$_2$	10.400
(L1)(H) $^{d)}$	9.334	(L1)(H)	9.303

$^{a)}$ Formation constants valid at I = 0.15 mol dm^{-3} in NaCl and T = 298.15 K; $^{b)}$ p M^{2+} + r H_2O = $M_p(OH)_r^{(2p-r)}$ + r H^+ ([74]; $^{c)}$ M^{2+} + L^- + H^+ = $MLH^{(2-1-1)}$ + H^+ (L = F^-; Cl^-) [74]; [73]; $^{d)}$ p H^+ + L^{n-} = $H_pL^{(-n+p)}$

From the knowledge of the speciation models of each system and their respective formation constants, it is possible, through the construction of distribution diagrams, to simulate the distribution of species at different concentrations and metal:ligand molar ratios (leachate in this case) and at different pHs.

As an example, Figure 52 reports the distribution diagram of the Cd^{2+}/P4 system.

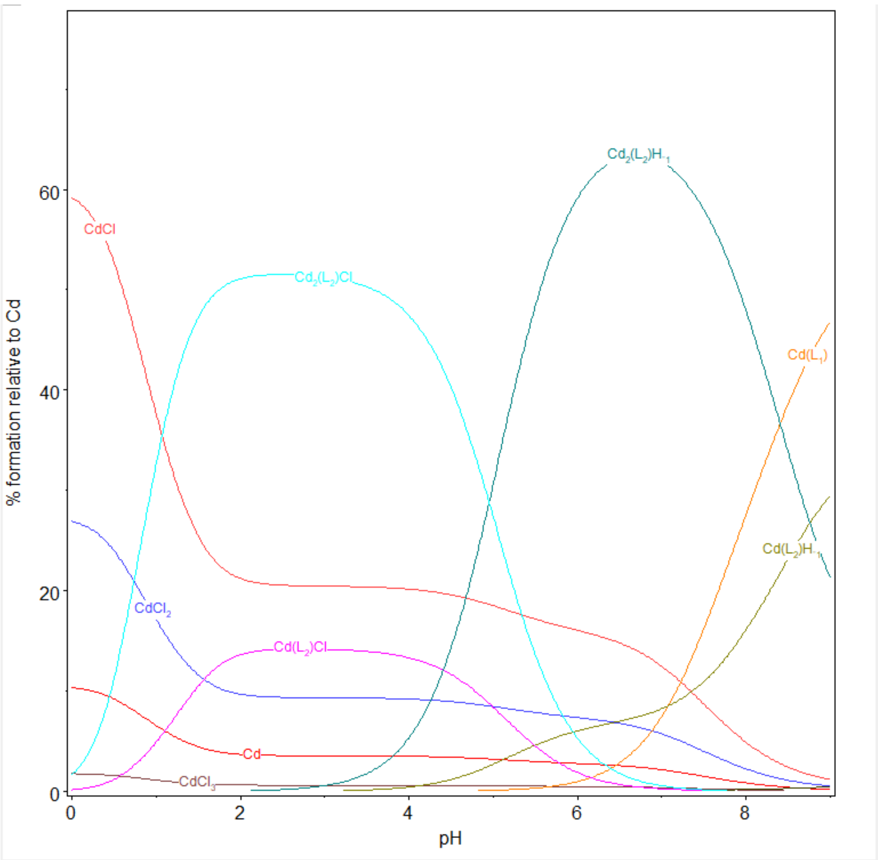


Figure 52: Distribution diagram of the Cd^{2+}/P4 system.

Experimental conditions: c_{Cd2+} = 1.57 mmol dm^{-3}; c_{L1} = 16.2 mmol dm^{-3}; c_{L2} = 0.6 mmol dm^{-3}; C_{Cl-} = 178.9 mmol dm^{-3}, at T = 298.15 K.

The distribution diagram in Figure 52 shows that in the pH range below 6, there is a clear prevalence of species involving carboxylic groups (L2), with the Cd_2(L2)OH species reaching over 60% formation at pH 6.5 and remaining present until pH ~8. The Cd(L2)OH species reaches almost 30% formation at pH ~8. The high chloride presence in the solution determines the occurrence of $CdCl_i$ species, mainly at acidic pH, avoiding the possible formation of hydrolytic metal species. As for ternary mixed species Cd^{2+}/percolate/chloride, they reach significant percentages at pH between 2 and 4.5, disappearing at pH ~6.5, where the Cd(L1) species begins to form, the only one involving the -OH group (L1).

Figure 53 reports the distribution diagram of the Cd^{2+}/P5 system. A different input model was used with respect to P4 sample, owing to the different acid-base properties and the different content of main components (for example, in the case of the P5 leachate, the protonated fluoride species and its complexation with Cd^{2+} wase not considered, since F^- was not determined in significant concentrations by the characterization analysis).

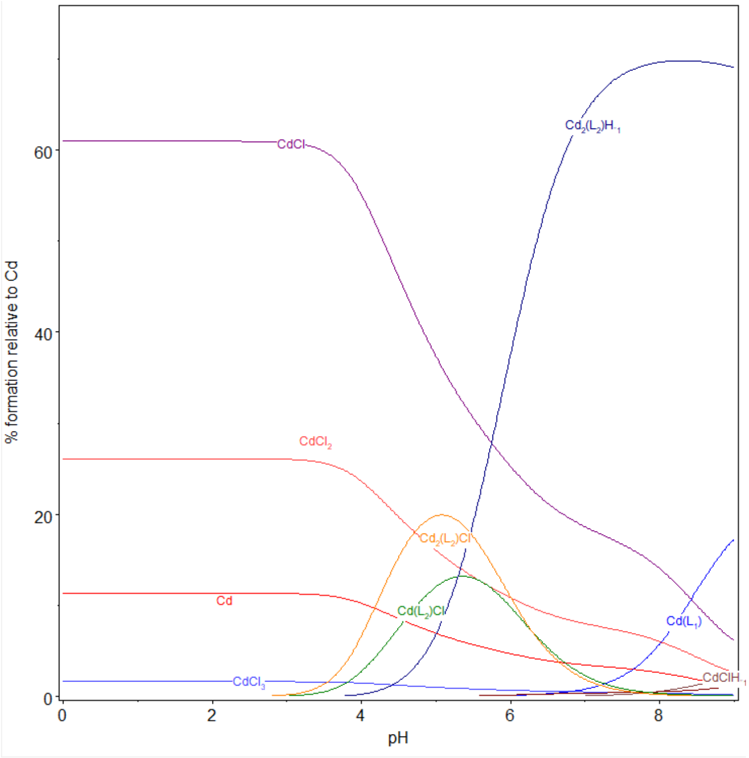


Figure 53: Distribution diagram of the Cd^{2+}/P5 system.

Experimental conditions: c_{Cd2+} = 0.50 mmol dm^{-3}; c_{L1} = 14.6 mmol dm^{-3}; c_{L2} = 0.28 mmol dm^{-3}; C_{Cl-} = 178.9 mmol dm^{-3}; T = 298.15 K.

A comparison of the Cd^{2+}/P5 distribution diagram with respect to the Cd^{2+}/P4 system, allows to observe a higher formation of CdCl$_i$ species whose formation percentages remain nearly constant until pH ~4, where the formation of species involving carboxylic groups is observed. The formation percentages of Cd(L2)Cl and Cd$_2$(L2)Cl species are lower than in the system with percolate P4 and show a formation percentage lower than 20% for the former and about 20% for the latter at pH ~5. Regarding the ternary hydrolytic Cd$_2$(L2)OH species, it reaches a maximum of 70% formation at pH = 8. As for the species involving the -OH group, it forms in a relatively low percentage and only at pH > 8. Again, the stability of the complexes inhibits the formation of the metal hydrolytic species, except for the ternary CdClOH species, which forms in very low percentages at pH ~9. Since it has been emphasized several times that the qualitative and quantitative composition of the leachate varies over time, to obtain information about the behavior of the metal/leachate systems, it is useful to simulate the different distribution of species at different concentrations of the components. For this reason, an additional species distribution diagram for the Cd^{2+}/P5 system was drawn at different metal:leachate molar ratios, as shown in Figure 54.

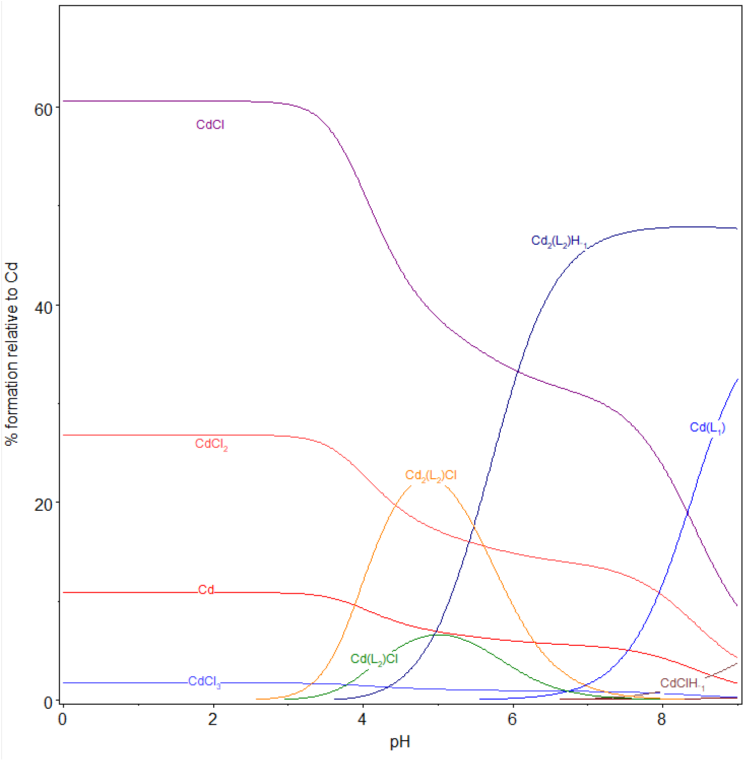


Figure 54: Distribution diagram of the Cd^{2+}/P5 system.

Experimental conditions: c_{Cd2+} = 1.16 mmol dm^{-3}; c_{L1} = 14.6 mmol dm^{-3}; c_{L2} = 0.28 mmol dm^{-3}, C_{Cl-} = 178.9 mmol dm^{-3}, a T = 298.15 K.

In this case, the formation percentages of $CdCl_i$ species remain fairly unchanged, unlike mixed metal-ligand species. It can be observed that the formation percentage of the Cd(L2)Cl species decreases, with a maximum falling below 10%. The same applies to the dimeric Cd_2(L2)OH species, which decreases to 50% but reaches its maximum at more acidic pH (pH=7). However, it is possible to notice that the Cd(L1) species, on the other hand, has higher formation percentages, reaching 30% at pH 9. The ternary hydrolytic species CdClOH is still present in small percentages at pH > 8.5. The information obtained from the distribution diagrams is essential as it provides insights into the prevalent species at a given pH and metal concentration. Indeed, due to their solubility, these species can be transported by the leachate through various environmental compartments, leading to potential contamination risks.

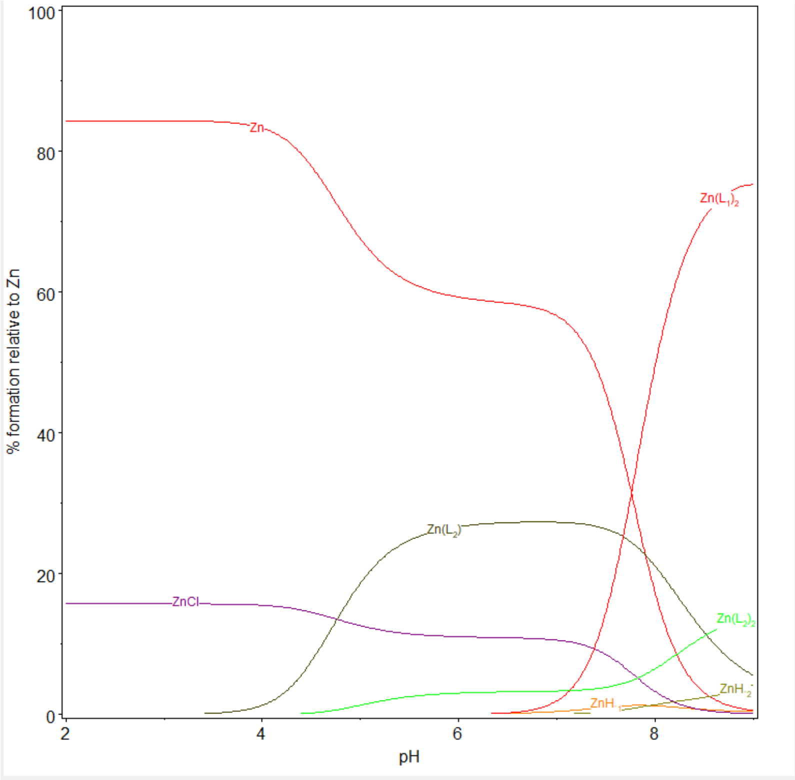


Figure 55: Distribution diagram of the Zn^{2+}/P4 system.

Experimental conditions: c_{Zn2+} = 0.47 mmol dm^{-3}; c_{L1} = 12.23 mmol dm^{-3}; c_{L2} = 0.16 mmol dm^{-3}, C_{Cl-} = 169.7 mmol dm^{-3}, a T = 298.15 K.

Figure 55 reports the distribution of the Zn^{2+}/P4 species. The lower stability of zinc complexes, compared to those with Cd^{2+}, allows the Zn^{2+} ion to be present in its free form for a significant part of the investigated pH range; for example, at pH ~7, it is present as a free ion at approximately 60%. Interaction with the leachate begins at pH ~4, with the presence of only the Zn(L2) species up to pH ~ 6.8, where the $Zn(L2)_2$ (~20%) and $Zn(L1)_2$ (~80%) species form. The $ZnCl^+$ species is also present up to pH ~8, as well as, albeit in low percentages, the hydrolytic $ZnOH^+$ and $Zn(OH)_2^0$ species.

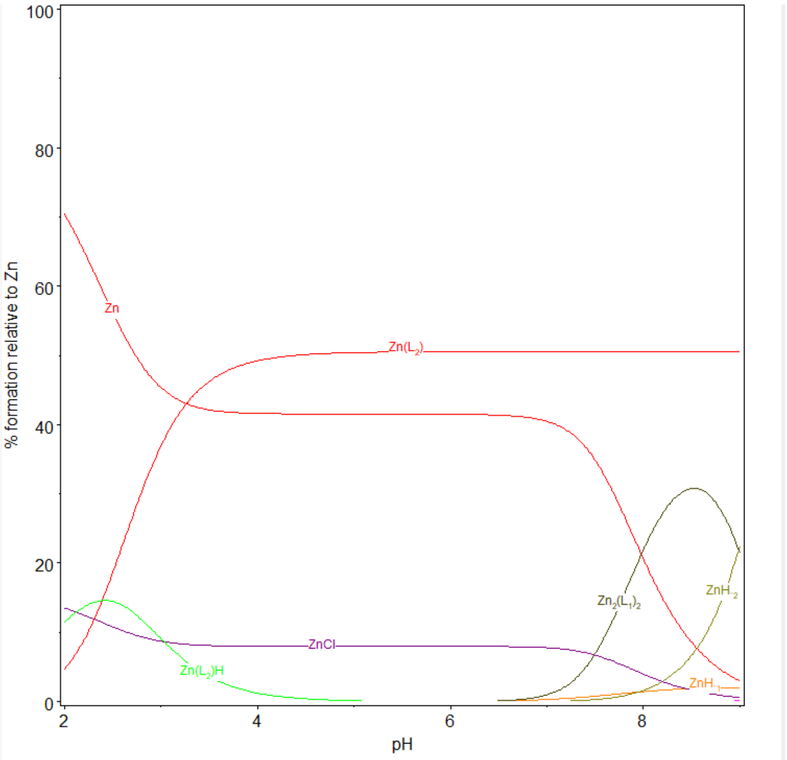


Figure 56: Distribution diagram of the Zn^{2+}/P5 system.

Experimental conditions: c_{Zn2+} = 0.95 mmol dm^{-3}; c_{L1} = 12.71 mmol dm^{-3}; c_{L2} = 0.48 mmol dm^{-3}, C_{Cl-} = 175 mmol dm^{-3}, at T = 298.15 K.

In the case of leachate P5 (Figure 56), we observe a different distribution compared to the Zn^{2+}/P4 system due to the different speciation model. In this case, we observe that the complexation starts at pH ~2 with the Zn(L2) and Zn(L2)H species that reach ~50% formation, while at pH 7, we observe the formation of the $Zn_2(L1)_2$ species reaching ~40% formation.

For Cu^{2+}, investigations were performed only on leachate P4; using the same approach applied to previous systems, the only model that allowed the best fitting of the e.m.f. (mV) vs. ml of titrant data is featured by the $Cu_2(L2)$ and $Cu(L1)_2$ species, whose formation constants are reported in Table 24, together with the speciation model used as input.

Figure 57 shows the corresponding distribution diagram, from which we can observe that complexation with Cu^{2+} starts at pH ~3, with the $Cu_2(L2)$ species that reaches over 90% of formation at pH ~6.8; after this pH values, the $Cu(L1)_2$ species prevails, reaching 95% at pH ~8.6. Below pH ~7, we observe the coexistence with the chlorinated species of Cu^{2+} and with the free metal. The formation of hydrolytic species of the metal is avoided.

Table 24: Speciation model and formation constants of the species reported in the input of the Cu^{2+}/P4 system, and formation constants of the Cu^{2+}/P4 species.

P4	
	log β_{pqr} $^{a)}$
kW	-13.740
(Cu)(OH)$^{b)}$	-7.7
$(Cu)_2(OH)$ $^{b)}$	-6.1
$(Cu)_2(OH)_2$$^{b)}$	-10.72
(Cu)(Cl) $^{c)}$	0.64
$(Cu)(Cl)_2$ $^{c)}$	0.6
(F)(H)$^{d)}$	2.960
$(F)_2(H)$ $^{d)}$	3.520
(L2)(H) $^{d)}$	7.820
$(L2)(H)_2$ $^{d)}$	12.640
(L1)(H) $^{d)}$	9.334
$Cu(L1)_2$	8.61±0.01$^{e)}$
$Cu_2(L2)$	11.5±0.04

$^{a)}$ Formation constants valid at I = 0.15 mol dm^{-3} in NaCl and T = 298.15 K; $^{b)}$ $p\ M^{2+} + r\ H_2O = M_p(OH)_r^{(2p-r)} + r\ H^+$ [74];$^{c)}$ $M^{2+} + i\ L^- = ML_i^{2-i)} + H^+$ ($L = Cl^-; F^-$) [73];$^{d)}$ $p\ H^+ + L^{n-} = H_pL^{(-n+p)}$ ($L = F^-$, L1 or L2); $^{e)}$ 95% Confidence Interval (C.I.)

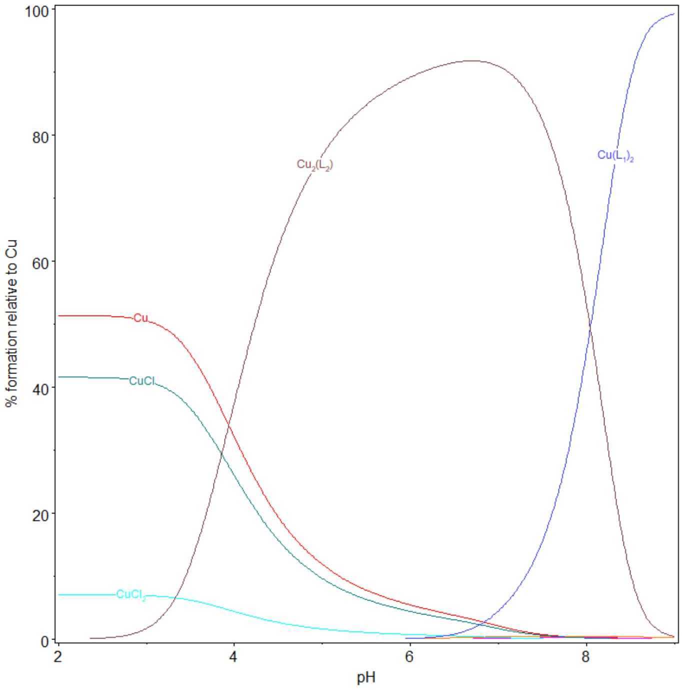


Figure 57: Distribution diagram of the Cu^{2+}/P4 system.

Experimental condition: c_{Cu2+} = 1.0 mmol dm^{-3}; c_{L1} = 15.80 mmol dm^{-3}; c_{L2} = 0.48 mmol dm^{-3}, C_{Cl-} = 189.6 mmol dm^{-3}

11.5 Voltammetric measurements on the Pb^{2+}/leachate

In order to have more experimental evidence of the complexing ability of leachate to interact with metals, despite being in an advanced methanogenic state, two series of voltammetric measurements were carried out, as outlined in the experimental section. In the first series, solutions containing individual metals (Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}) were prepared at known concentrations (ranging from 10^{-6} to 10^{-7} mol dm^{-3}) in $NaNO_3$ ~0.15 mol dm^{-3} and underwent a potential scan in a voltage range E/V dependent on their discharge potential on the working electrode. Subsequently, small aliquots of a 1:25 diluted leachate solution of approximately 100 – 150 µl were added, and a new scan was performed after each addition. Observing Figures 58-60, which represent individual differential voltammetric curves for Pb^{2+}, Cd^{2+} and Cu^{2+}, several considerations can be made. Firstly, a decrease in current intensity (i/A) proportional to each addition of leachate can be noted, which cannot be attributed to dilution effects since the added solution volumes are minimal. Additionally, a shift in discharge potentials is observed upon the addition of various leachate aliquots, indicating the complexation process of the metal by the leachate itself.

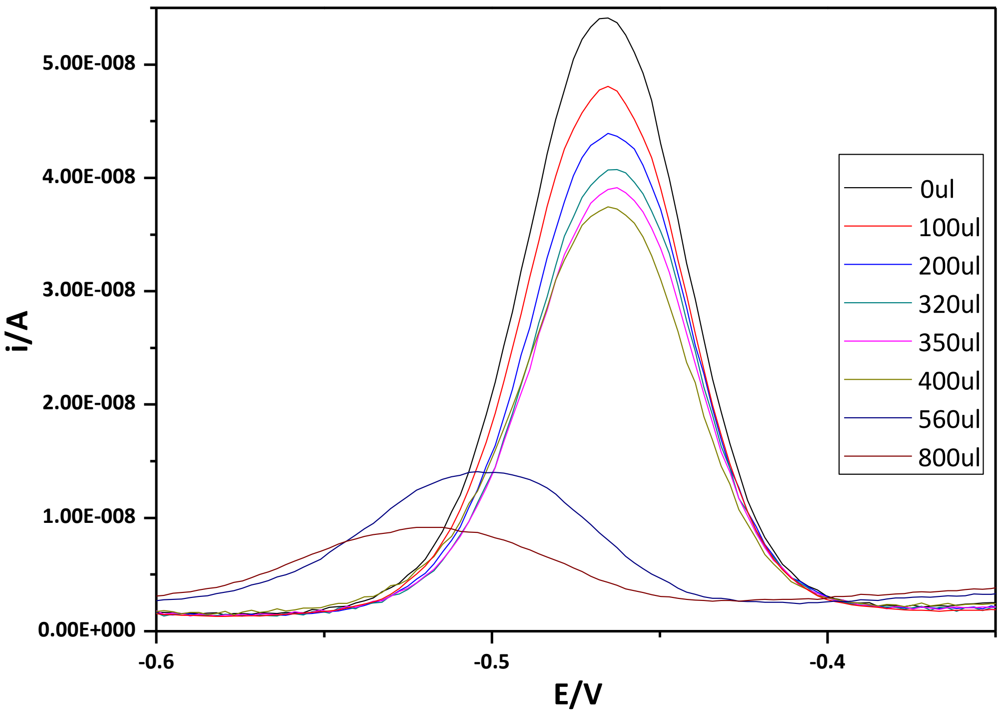


Figure 58: Voltammograms of a solution containing Pb^{2+} at an initial concentration of 7.6 x 10^{-7} mol dm^{-3}, to which successive aliquots of 100-150 ml of leachate (P4) diluted in a 1:25 ratio were added, at T = 298.15 K.

These observations were noted for all the studied metals. Particularly, since the current intensity measured after the addition of each leachate aliquot is correlated with the amount of free metal, the greater variation observed for Pb^{2+}, between the initial and final current intensity values (A), and hence the lower final concentration, is undoubtedly an indicator of a higher sequestering capacity for this metal compared to the others investigated.

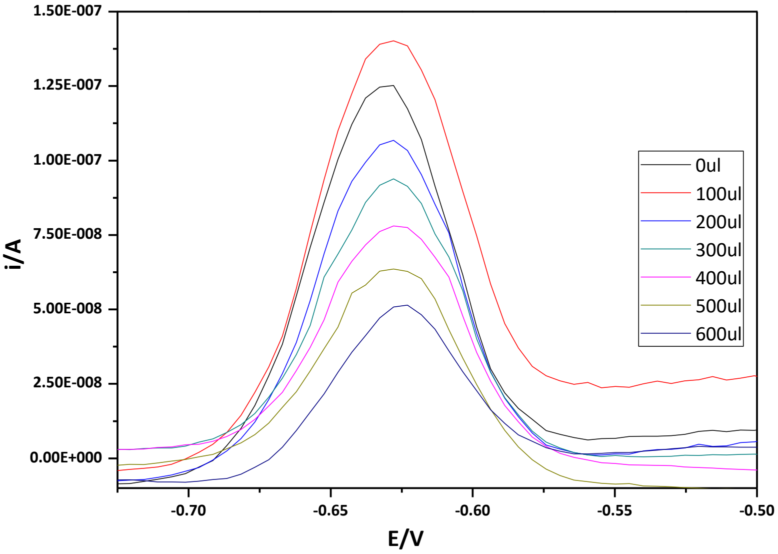


Figure 59: Voltammograms of a solution containing Cd^{2+} at an initial concentration of 1 x 10^{-6} mol dm^{-3}, to which successive aliquots of 100-150 ml of leachate (P4) diluted in a 1:25 ratio were added, at T = 298.15 K.

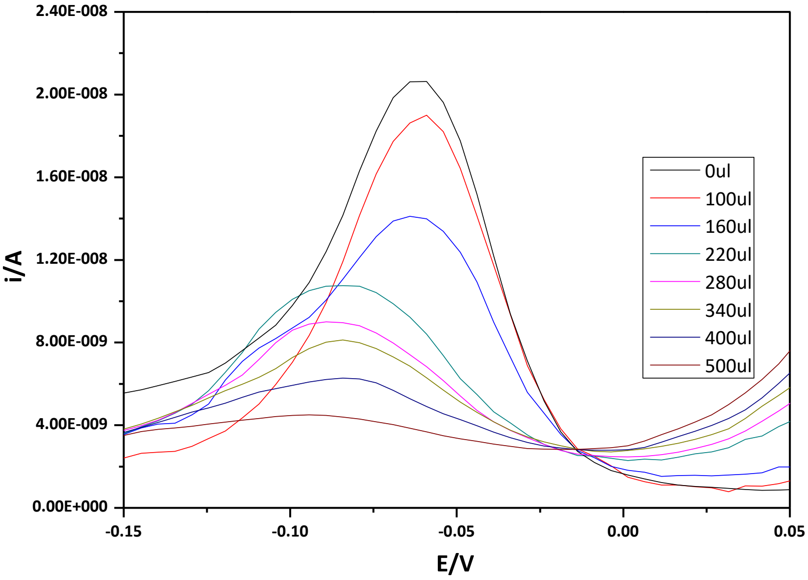


Figure 60: Voltammograms of a solution containing Cu^{2+} at an initial concentration of 1 x 10^{-6} mol dm^{-3}, to which successive aliquots of 100-150 ml of leachate (P4) diluted in a 1:25 ratio were added, at T = 298.15 K.

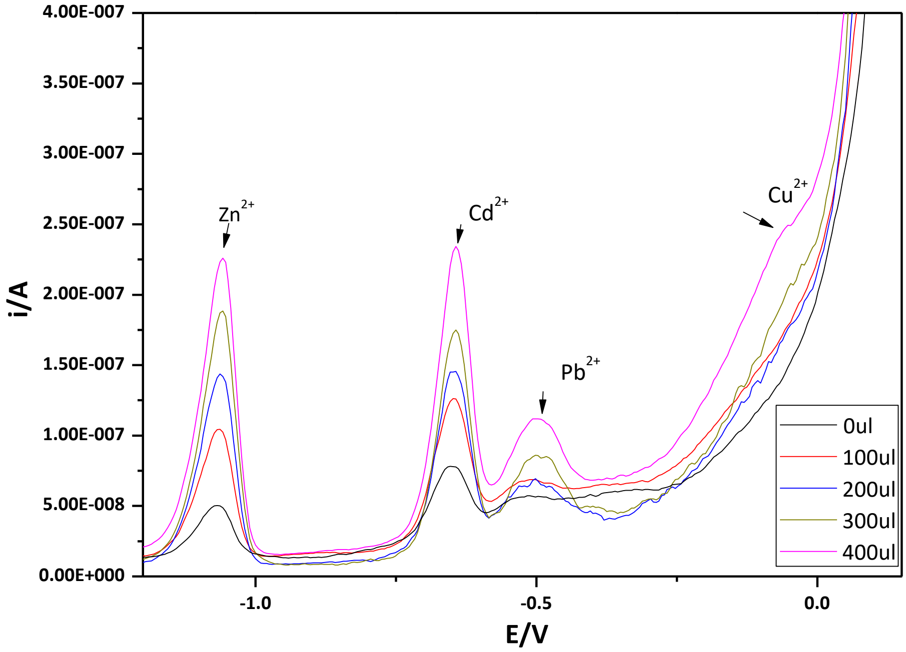


Figure 61: Voltammograms of a solution containing leachate (P4) diluted in a 5:25 ml ratio with $NaNO_3$ 0.1 mol dm^{-3}, at T = 298.15 K, to which successive aliquots of 100 ml of a mixture containing: Zn^{2+} (6.1 x 10^{-7} mol dm^{-3}); Cd^{2+} (3.56 x 10^{-7} mol dm-3); Pb^{2+} (1.93 x 10^{-7} mol dm^{-3}); Cu^{2+} (6.28 x 10^{-7} mol dm^{-3}) were added.

The second series of measurements involved preparing solutions containing leachate P4 diluted in a 1:25 ratio in $NaNO_3$ 0.15 mol dm^{-3} to stabilize the charge migration. To this prepared solution, aliquots of a mixture containing the metals Zn^{2+} (c_{Zn} = 6.1 x 10^{-7} mol dm^{-3}), Cd^{2+} (c_{Cd} = 3.56 x 10^{-7} mol dm^{-3}), Pb^{2+} (c_{Pb} = 1.93 x 10^{-7} mol dm^{-3}), and Cu^{2+} (c_{Cu} = 6.28 x 10^{-7} mol dm^{-3}) were added. The choice to use $NaNO_{3(aq)}$ instead of $NaCl_{(aq)}$, as already made for the potentiometric titrations, is due to the possible formation of insoluble Pb^{2+}salts with Cl^- and the presence of Pb^{2+} as a trace in the NaCl salt lot.

In Figure 61, the differential voltammogram of the solution containing the percolate P4 diluted in a ratio of 1:25 in $NaNO_3$ 0.15 mol dm^{-3} with the four metals is shown.

The first scan, in black, shows how the studied metals (Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+}) are naturally present in the leachate. For the subsequent additions of 100 µl of the metal mix, an increase in current intensity for each analyte is observed, as expected because even if part of the added metal tends to be complexed by the leachate, the quantity reduced due to the RedOx process is negligible compared to its analytical concentration. What indicates the complexation has occurred is the shift of the peaks in each curve.

By processing the voltammetric measurements and the LIANA program, it was possible to define a speciation model for the Pb^{2+}/P4 system, which could not be studied by potentiometry due to the formation of sparingly soluble species at pH = 2.5.

The peak potential shift was interpreted with the formation of labile complex species [75] [76], at a given pH value, by means:

$$\Delta E_p = E_{\mathrm{p}}^{\mathrm{Free}} - E_{\mathrm{p}}^{\mathrm{Compl}} = \frac{RT}{nF}\ln\frac{c_{\mathrm{M}}}{[M]} + \frac{RT}{nF}\ln\frac{\mathrm{i}_{\mathrm{p}}^{\mathrm{Free}}}{\mathrm{i}_{\mathrm{p}}^{\mathrm{Compl}}} \tag{11.1}$$

where E_p is the potential peak of the free and complexed metal; i_p is the current intensity of the metal and of the metal in presence of the ligand; c_M and $[M]$ are the analytical and the free metal concentration, respectively. The potential peaks and the current intensities are directly determined from the experimental data, whereas $c_M/[M]$ are calculated by the mass balance equations. Considering the low metal concentrations and high ligand, the assumption that no polynuclear species were formed is reasonable.

The studied pH range is limited due to the absence of inorganic acid in the solution, ranging from pH ~4 to pH ~8. For this reason, only the monomeric fraction containing carboxylic groups (L2) is involved in possible interactions with Pb^{2+}. The speciation model considered the hydrolytic species of the metal and the protonations of ligand L2, and the results are summarized in Table 25, highlighting the formation of two species, Pb(L2) and Pb(L2)OH.

Table 25: Formation constants of the P4 leachate species with Pb^{2+} in $NaNO_{3(aq)}$ at I = 0.15 mol dm^{-3} and T = 298.15 K

Leachate	Species [a]	
	logβ Pb(L2)	logβ Pb(L2)OH
P4	8.61±0.10 [b]	1.54±0.09

[a] Equilibrium: $Pb^{2+} + (L2)^{2-} + r\,H_2O = Pb(L2)OH_r^{(-r)} + H^+$; [b] 95% Confidence Interval (C.I.)

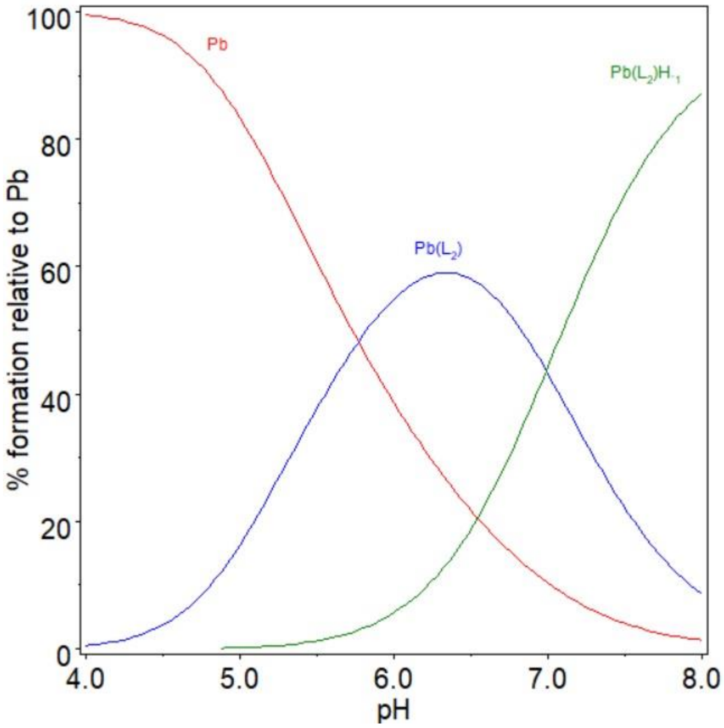


Figure 62: Distribution diagram of the Pb^{2+}/P4 species in $NaNO_{3(aq)}$ at I = 0.15 mol dm^{-3} and T = 298.15 K. Experimental conditions: c_{Pb2+} = 7.6 · 10^{-7} mol dm^{-3} and $c_{(L2)}$ = 7.6 · 10^{-7} mol dm^{-3}.

In Figure 72, the distribution diagram shows that the Pb(L2) and Pb(L2)OH complexes achieve high formation percentages, namely, ~60 and 85%, at pH ~6.3 and 8.0, respectively.

11.6 Sequestering ability

In many fields where binding equilibria are involved in crucial processes, several aspects must be taken into account in the choice of the "best" chelant. The ideal "chelant" should form very stable complexes "in competition with the stability of endogenous ligands in the body" and should be selective "toward the target metal ion" [77]. These characteristics are dependent on the stability of the complexes formed by the potential chelant and the target metal ion, but also on that of "side species", *i.e.* those formed by other ligands with the target ion and those by the potential chelant with other ions. The efficacy of the chelation also depends on the competitive reactions, involving simultaneous equilibria in different conditions; as an example, considering a very simple one metal-one ligand system in aqueous solution (and this is never the case of real systems), one must at least take into account the competition of H^+ with the ligand and OH- with the metal. This means that the selectivity and the whole "sequestering" ability of a chelant toward a cation, as well as the comparison between two or more chelants, cannot be easily assessed by the simple analysis of single sets of stability constants of metal/ligand complexes in real conditions, especially if “different complex species are formed rather than a single prevailing one” [78] [79]. In the past, some procedures were proposed for the quantification of the sequestering ability of a given ligand toward metal ions; as an example, the free metal concentration in solution at equilibrium, expressed as pM, is one of the most used parameters in chelation therapy to assess the binding ability of various chelants toward a given metal. Nevertheless, it has been frequently pointed out that the use of pM for comparisons may be, sometimes, “problematic”, so that its use by “non experts” should be discouraged.

To overcome this problem, many years ago the $pL_{0.5}$ parameter [80] was proposed, that is an easy-to-use and easy-to-get instrument to make fast and reliable quantifications of the sequestering ability of a ligand toward a given component (not necessarily a metal cation). The $pL_{0.5}$ parameter, represents the total ligand concentration necessary to sequester 50% of a given metal ion present as trace in given conditions, even in the presence of other components. It is rapidly calculated in a very simple way by the most common programs used to plot the speciation diagrams.

The $pL_{0.5}$ is then obtained graphically, or by fitting plotted data with the following equation.

$$\chi = \frac{1}{1 + 10^{(pL - pL_{o.5})}} \tag{11.2}$$

where χ is the fraction of the metal M (presents in trace) complexed by the ligand. The parameter $pL_{0.5}$, calculated by least squares analysis, gives the conditions for which 50% of metal is complexed by the ligand ($[L]_{tot} = 10^{-pL0.5}$) and can be calculated once the conditions (pH, ionic strength, supporting electrolyte, temperature) are fixed and gives an objective representation of the binding ability. This function is assimilable to a sigmoid curve (or a dose response curve) with asymptotes of 1 for pL → -∞ and 0 for pL → +∞. It is important to note that: this property varies with the experimental conditions, but it is independent of the analytical concentration of the metal ion when this is present as a trace amount in the system.

In particular cases, the $pL_{0.5}$ is numerically equivalent to other parameters used for the same purposes, like the intrinsic median binding concentration, BC_{50} [81] [82] [83] [84] or the historical Schwarzenbach’s apparent formation constant [85].

Despite the apparent redundancy and uselessness of a new parameter to quantify the sequestering ability of a ligand toward a metal cation, it must be underlined here that $pL_{0.5}$ shows some advantages in its use, which enable it to be of more immediate use for not-specialists. For example, like any other stability constant, the higher the $pL_{0.5}$, the higher the sequestering ability of the ligand, and this is usually of more immediate comprehension, while this is not the case for BC_{50}, which specifically designed to be similar to the median inhibitory concentration IC_{50}. However, the greatest advantage of the use of $pL_{0.5}$ is probably that related to its determination: i) as already pointed out, $pL_{0.5}$ can be calculated easily by means of very common programs and does not require any particular skills in the treatment of simultaneous equilibria and/or the solution of systems of mass balance equations.

This parameter changes with varying experimental conditions (such as ionic strength, pH, temperature, and ionic medium) but is independent of the metal concentration when it is present in traces (~10^{-12} mol dm^{-3}).

In the examined case, the $pL_{0.5}$ was calculated at different pH values for the investigated metal-percolate systems. pH was chosen to be varied because this parameter in multicomponent solutions, as in the case of leachate, undergoes variations over time and necessarily changes if there is infiltration into groundwater or surface water, undergoing dilution.

Table 26: Values of $pL_{0.5}$ calculated at different pH levels for the leachates P4 and P5, at T = 298.15 K.

	P4	P5		P4	P5		P4
	Cd^{2+}			Zn^{2+}			Cu^{2+}
pH			pH			pH	
3	4.42	-	-	-	-	-	-
4	6.38	0.26	4	-	3.97	4	-
5	8.16	1.52	5	1.71	5.23	5	-
6	9.75	2.42	6	2.89	6.12	6	0.84
7	10.30	2.84	7	3.86	6.54	7	1.82
8	10.36	2.92	8	4.48	6.57	8	2.66
9	10.36	2.91	9	4.02	5.71	9	3.14
10	10.36	2.56	-	-	-	-	-

Also, in the calculation of $pL_{0.5}$, the organic matter contained in the leachate was considered to consist of two repetitive units assimilable to two ligands, as defined by the application of the Polyprotic Like Model. The pL values reported on the x-axis are considered as the sum of the two ligands, L1 and L2, maintaining, for each point of the simulation, the same concentration ratio of L2/L1 determined experimentally.

Figures 63 and 64 report the sequestering ability of leachates P4 and P5, respectively, at different pH values against Cd^{2+}. In both systems, an increase in pH corresponds to an increase in the $pL_{0.5}$ value.

However, there is a clear difference in sequestering ability, more pronounced as the pH becomes more alkaline.

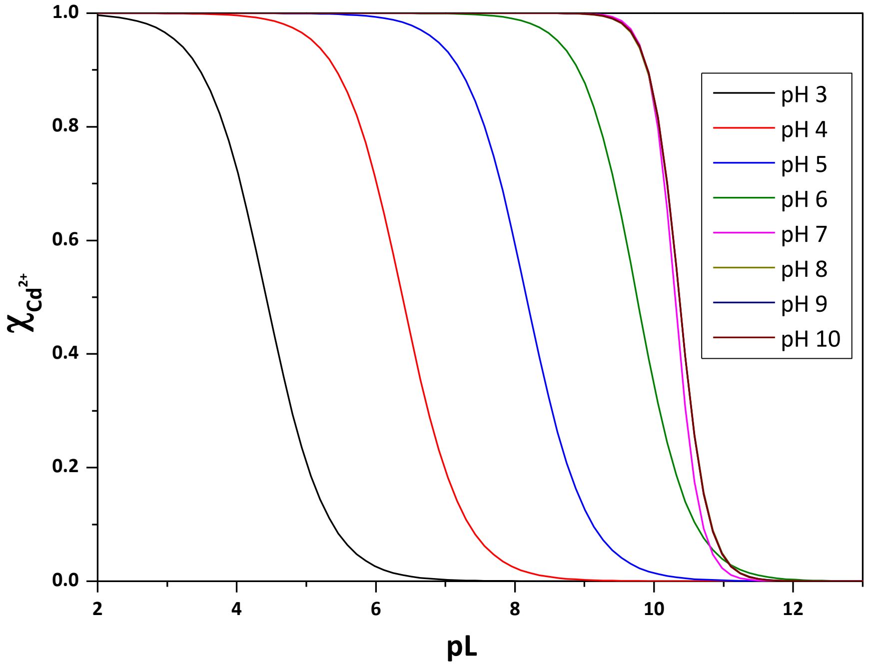


Figure 63: Sequestering ability of leachate P4 against Cd^{2+} at different pH values and T = 298.15 K.

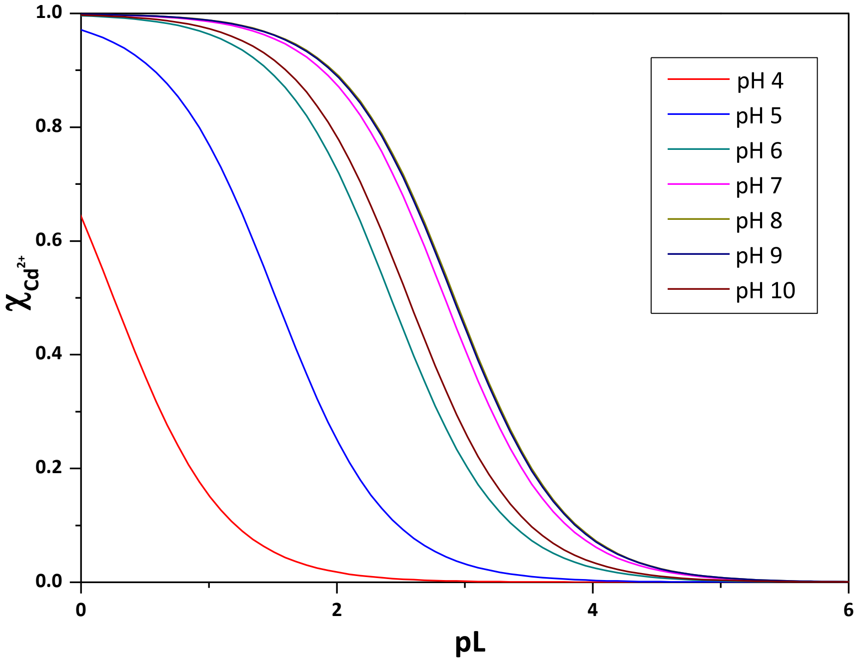


Figure 64: Sequestering ability of leachate P5 against Cd^{2+} at different pH values and T = 298.15 K.

In Table 26, the $pL_{0.5}$ values at different pH values for each system are reported. It is possible to explain the differences between the values, with the same metal, considering the different stabilities of metal:leachate complex species. Specifically, for Cd^{2+}, leachate P4 presents a higher concentration of -COOH groups compared to P5, especially in the leachate sampled in November 2021.

Figures 65 and 66 instead show the sequestering ability of leachates P4 and P5 against Zn^{2+} at different pH values. Referring to Table 26, it can be observed that the $pL_{0.5}$ values for leachate P4 are lower, at the same pH, compared to the system with Cd^{2+}; on the contrary, the values for the P5/Zn^{2+} system are higher than the P5/Cd^{2+} system. Due to the different speciation models between the two systems with Zn^{2+}, it is difficult to associate this trend with a specific factor. However, if we observe the value of the only common species to the two systems, in the case of leachate P5, the formation constant of the M(L2) species is about two orders of magnitude higher than the analogous one with P4. Furthermore, the decrease in the $pL_{0.5}$ value for the Zn^{2+}/P5 system after pH = 7 may be due to the low percentage of formation of species involving the -OH group and ligand L1.

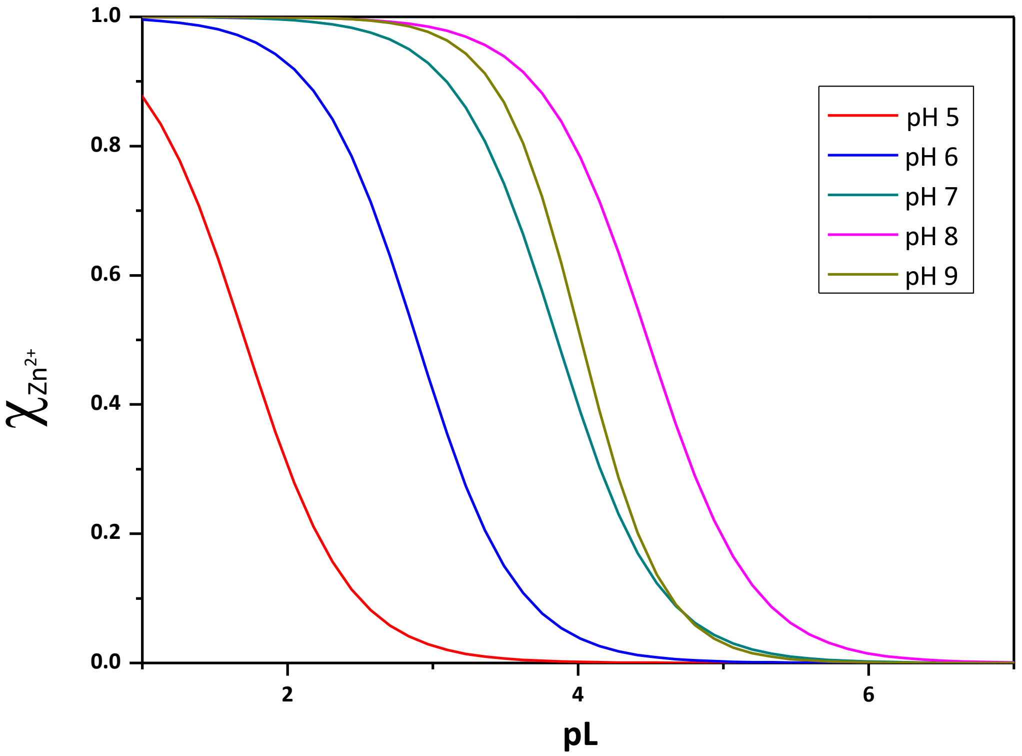


Figure 65: Sequestering capacity of leachate P4 towards Zn^{2+} at different pH values and T = 298.15 K.

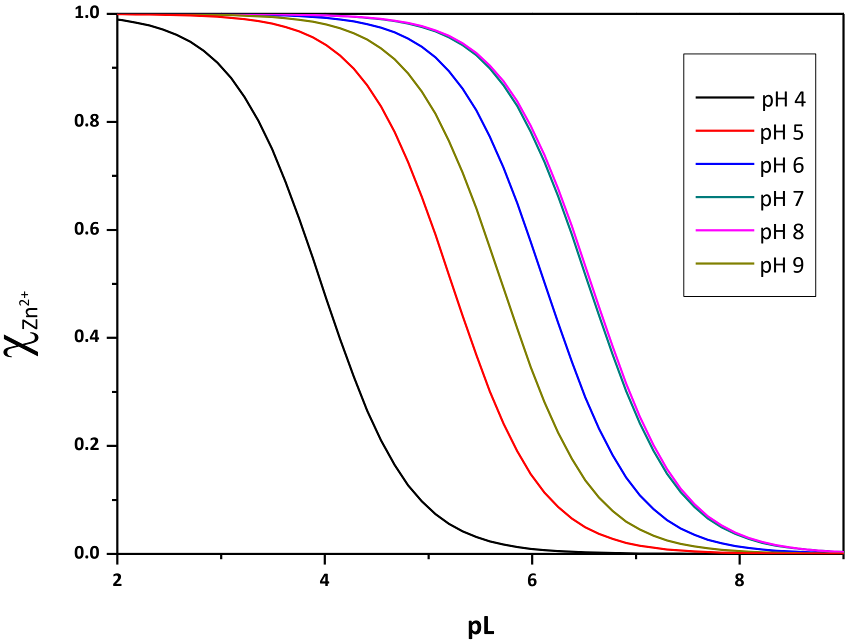


Figure 66: Sequestering ability of leachate P5 towards Zn^{2+} at different pH values and T = 298.15 K.

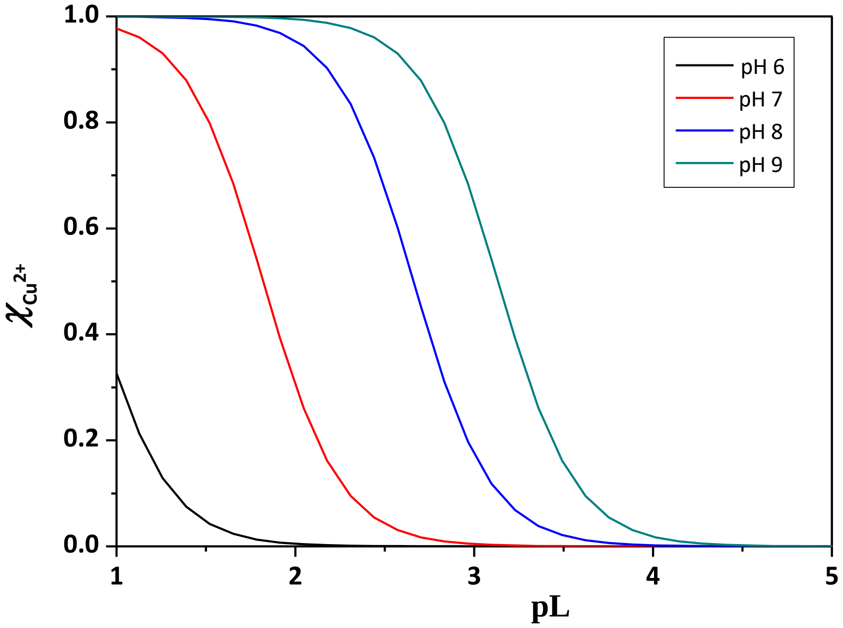


Figure 67: Sequestering ability of leachate P4 towards Cu^{2+} at different pH values and T = 298.15 K.

Figure 67 shows how the sequestering ability of leachate P4 varies with pH concerning Cu^{2+}. As observed in other systems, $pL_{0.5}$ (see also Table 26) tends to increase with increasing pH, although the values are relatively low compared to other copper-metal ligand systems. The low values, especially at lower pH, are justified by the prevalence of copper complexes with chloride in that range, whose distribution and formation percentage vary depending on the metal concentration.

12 Conclusion

The primary outcomes derived from the investigations concerning the characterization and determination of thermodynamic properties, including acid-base behavior and complexation with some metals, of landfill leachates can be succinctly outlined as follows:

1. Sampling of municipal solid waste (MSW) landfill leachates was conducted from piezometers situated within the landfill body, employing low-flow dynamic sampling following appropriate purging. Additional samples of leachate-contaminated water were collected from piezometers located in the proximity and outside the landfill.
2. The characterization of the leachates was executed in accordance with the guidelines provided in Table 2 of Annex 5, Part IV of the Italian Legislative Decree 152/2006.
3. Chemical characterization of the leachates was carried out using official analytical methods (UNI EN ISO, EPA, APAT-CNR methods). For numerous analytes, it was observed that their concentrations surpassed the contamination limits specified in Table 2 of the Italian Legislative Decree 152/2006.

Notably, only a few instances of exceedances were noted for organic components in piezometers located within the landfill body.

4. Analytical findings revealed distinct variations in the qualitative and quantitative composition of leachates collected during two distinct periods: November 2021 and June 2022. These periods are characterized by disparate levels of rainfall and water influx into the landfill body. Generally, an increase in rainfall corresponded to a decrease in the concentrations of potential contaminants. This phenomenon can be attributed to the dissolution mechanisms of contaminants, where the dissolving effect in the aqueous phase is a primary factor. However, during winter periods with higher rainfall, a dilution effect complements the dissolving process.
5. The characterization of leachates was further conducted using ATR-IR and SEM-EDX. ATR-IR analyses, performed on both dried and calcined samples, evidenced the predominant functional groups in each leachate. Prominent bands were identified, primarily associated with carbonyl and carboxyl groups, along with distinct signals linked to -OH groups. Notably, no intense bands corresponding to -NR functional groups (where R = H or alkyl groups) were observed. The presence of these functional groups can be attributed to organic matter dissolved in the leachate, resilient to biodegradation processes occurring throughout the landfill's various digestion stages (both aerobic and anaerobic).
6. Considering that leachates comprise a blend of inorganic and organic matrices, the intricate ATR-IR spectra may arise from signal overlap due to the simultaneous presence of various functional groups (organic and/or inorganic) in the mixture. Consequently, similar investigations were replicated on aliquots obtained post-calcination, primarily composed of inorganic components like $C\text{-}NO_x$, C-SR (R = O, H), $C\text{-}P\text{-}O_x$, etc. Results affirmed our hypotheses, confirming that in dried samples, the spectra were a product of overlapping bands. Specifically, calcined leachate samples from P5 revealed the presence of bands associated with residues containing phosphorus, with a notable concentration of phosphate anions in the P5 leachate.
7. SEM-EDX analyses corroborated the prevalence of carboxyl/carbonyl and -OH groups in the leachate's functional groups, while groups related to nitrogen and sulfur were found to be negligible. EDX analyses further validated these findings by quantifying the percentages of macroelements in both dried and calcined samples.
8. The determination of thermodynamic properties, specifically protonation and metal complexation constants of the leachates, was carried out using the simplified PolyProtic Like Model. Two distinct approaches were employed, each considering a different number of functional groups per repeating unit. Both approaches are deemed equally valid, and the selection between them hinges on the quantity of carboxylic and alcohol/phenolic groups established through acid-base titration for each leachate.

9. From a complexation standpoint, each leachate exhibited unique behavior influenced by its acid-base properties and the concentration of carboxylic and -OH groups. different speciation models were checked, revealing diverse species stabilities. Notably, the complexes formed by Cd^{2+} with the two studied leachates demonstrated considerable stability in terms of interaction strength. Comparatively, the complexes formed by the P4 leachate exhibited higher stability than those formed by P5. Concerning Zn^{2+}, the only shared M(L2) species displayed greater stability in the P5 leachate compared to P4. For Pb^{2+}, investigations were carried out by voltammetric titrations (only for P4).
10. The quantification of the effective interaction strength between leachates and metals was estimated through the parameter $pL_{0.5}$. A notable variation in behavior among the leachates, particularly concerning Cd^{2+}, was evident. Specifically, the P4 leachate exhibited a superior ability to sequester this metal compared to P5. In the case of Zn^{2+}, an inverse pattern was observed, wherein P5 demonstrated a higher sequestering capability compared to P4.

The results obtained from these investigations highlight the importance of knowing both from a qualitative and quantitative point of view the composition of the leachates produced by a MSW landfill, since in dependence on their different composition they tend to behave (in dependence of the acid-base and complexing properties) as carriers of contaminants through the soil and towards groundwater, with the consequent problems of contamination and/or environmental disaster and risks for the human health.

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14 Appendices

14.1 Appendix 1: Characterization plan’s analytical sets and tables

Table a: Standard parameter and methods for soil characterization

Soil analysis referring to D.Lgs. 152/2006 Table 1, Annex 5, part IV	
Parameter	**Analysis and extraction method**
Inorganic compound	DM 13/09/1999 SO n 185 GU n 248 21/10/1999 Met XI.1 + UNI EN 16170:2016
Antimony	UNI EN 15192 2020
Arsenic	
Beryllium	
Cadmium	
Cobalt	
Total chromium	
Chromium VI	
Mercury	
Nichel	
Lead	
Copper	
Selenium	
Thallium	
Vanadium	
Zinc	
BTEX	EPA5021 A2014- EPA 8260D2018
Benzene	
Ethylbenzene	
Styrene	
Toluene	
Xylene	
Sum of organic aromatic	
Carcinogenic chlorinated Aliphatic	EPA5021 A2014- EPA 8260D2018
Chloromethane	
Dichloromethane	
Trichloromethane	
Vinyl chloride	
1,2-Dichloroethane	
1,1 Dichloroethylene	
Trichloroethylene	
Tetrachloroethylene (PCE)	
Non-carcinogenic chlorinated aliphatics	EPA5021 A2014- EPA 8260D2018
1,1- Dichloroethane	
1,2-Dichloroethylene	
1,2-Dichloropropane	
1,1,2-Trichloroethane	
1,2,3-Trichloropropane	
1,1,2,2-Tetrachloroethane	

1,2-Dichloropropane	
Non-chlorinated phenols	EPA3546 2007 - EPA8270E 2018
Methyl phenol (o$^-$,m$^-$,p$^-$)	
Phenol	
Chlorinated phenols	EPA3546 2007 - EPA8270E 2018
2-chlorophenol	
2,4-dichlorophenol	
2,4,6-trichlorophenol	
Pentachlorophenol	
Hydrocarbons	
Light hydrocarbons C≤12	EPA 5021 A 2014 - EPA8015 C 2007
Heavy hydrocarbons C>12	UNI EN ISO 16703 2011

Table b: Standard parameter and methods for groundwater characterization

Groundwater analysis referring to D.Lgs. 152/2006 Table 2, Annex 5, part IV	
Parameter	**Analysis and extraction method**
Metals	UNI EN ISO 17294-2:2016
Aluminium	
Antimony	
Silver	
Arsenic	
Beryllium	
Cadmium	
Cobalt	
Total Chromium	
Chromium VI	EPA 7199 1996
Iron	
Mercury	
Nichel	
Lead	
Copper	
Selenium	
Manganese	
Thallium	
Zinc	
Inorganic pollutant	UNI EN ISO 17294-2:2016
Boron	
Fluorides	APAT CNR IRSA 4020 Man 29 2003
Nitrate	
Sulphate	
BTEX	EPA 5021 A 2014 + EPA 8260D 2018
Benzene	
Ethylbenzene	
Styrene	
Toluene	

Para-Xylene	
Carcinogenic chlorinated Aliphatic	EPA 5021 A 2014 + EPA 8260D 2018
Chloromethane	
Trichloromethane	
Vinyl chloride	
1,2-Dichloroethane	
1,1 Dichloroethylene	
Trichloroethylene	
Tetrachloroethylene (PCE)	
Hexachlorobutadiene	
Sum of organohalogenated	
Non-carcinogenic chlorinated Aliphatic	
1,1- Dicloroetano	EPA 5021 A 2014 + EPA 8260D 2018
1,2-Dicloroetilene	
1,2-Dicloropropano	
1,1,2-Tricloroetano	
1,2,3-Tricloropropano	
1,1,2,2-Tetracloroetano	
Pesticides	EPA3510 C 1996 +EPA 8081 B 2007
Alachlor	
Aldrin	
Atrazine	
alfa- hexachlorohexane	
beta-hexachlorohexane	
gamma-hexachlorohexane (lindane)	
Chlordane	
DDD,DDT,DDE	
Dieldrin	
Endrin	
Sum of pesticides	
Other substances	
Total hydrocarbons (expressed as n-hexane)	EPA 5021 A 2014 + EPA8015 C 2007 + UNI EN ISO9377 - 2 2002
Microbiologic	
Coliforms	APAT CNR IRSA 7010C
Fecal Streptococci	APAT CNR IRSA 7040C

Table c: Standard parameter and methods for superficial water characterization

Superficial waters analysis referring to D.M. April 14 2009, n°56 Tables 1/A e 1/B	
Parameter	**Analysis and extraction method**
Metalls	UNI EN ISO 17294-2:2016
Aluminium	
Antimony	
Silver	

Arsenic	
Beryllium	
Cadmium	
Cobalt	
Total Chromium	
Chromium VI	EPA 7199 1996
Iron	
Mercury	
Nichel	
Lead	
Copper	
Selenium	
Manganese	
Thallium	
Zinc	
Inorganic pollutant	
Boron	UNI EN ISO 17294-2:2016
Fluorides	APAT CNR IRSA 4020 Man 29 2003
Sulphates	APAT CNR IRSA 4020 Man 29 2003
BTEX	EPA 5021 A 2014 + EPA 8260D 2018
Benzene	
Ethylbenzene	
Styrene	
Toluene	
Para-Xylene	
Carcinogenic chlorinated Aliphatic	EPA 5021 A 2014 + EPA 8260D 2018
Chloromethane	
Trichloromethane	
Vinyl chloride	
1,2-Dichloroethane	
1,1 Dichloroethylene	
Trichloroethylene	
Tetrachloroethylene (PCE)	
Hexachlorobutadiene	
Sum of organohalogenated	
Non-carcinogenic chlorinated Aliphatic	EPA 5021 A 2014 + EPA 8260D 2018
1,1- Dichloroethane	
1,2-Dichloroethylene	
1,2-Dichloropropane	
1,1,2-Trichloroethane	
1,2,3-Trichloropropane	
1,1,2,2-Tetrachloroetane	
Pesticides	EPA3510 C 1996 +EPA 8081 B 2007
Alachlor	
Aldrin	

Atrazine	
alfa- hexachlorohexane	
beta- hexachlorohexane	
gamma- hexachlorohexane (lindane)	
Chlordane	
DDD, DDT, DDE	
Dieldrin	
Endrin	
Som of pesticides	
Other substances	
Total hydrocarbons (expressed as n-hexane)	EPA 5021 A 2014 + EPA8015 C 2007 + UNI EN ISO9377 - 2 2002
Chlorides	APAT CNR IRSA 4020 Man 29 2003
Nitrate	APAT CNR IRSA 4020 Man 29 2003
Microbiologic	
Total Coliforms	APAT CNR IRSA 7010C
Fecal Streptococci	APAT CNR IRSA 7040C

Table d: Standard parameter and methods for leachate characterization

Leachate analysis	
Parameter	**Analysis and extraction method**
Metals	
Aluminium	UNI EN 13657:2004, UNI EN 16170:2016
Antimony	
Silver	
Arsenic	
Beryllium	
Cadmium	
Cobalt	
Total Chromium	
Chromium VI	EPA 7199 1996
Iron	
Mercury	
Nichel	
Lead	
Copper	
Selenium	
Manganese	
Thallium	
Zinc	
Inorganic pollutants	
Nitrate	APAT CNR IRSA 4020 Man 29 2003
Nitrite	
Sulphates	
BTEX	

Benzene	EPA5021 A2014- EPA 8260D2018
Ethylbenzene	
Styrene	
Toluene	
Para-Xylene	
Carcinogenic chlorinated Aliphatic	
Chloromethane	EPA5021 A2014- EPA 8260D2018
Trichloromethane	
Vinyl chloride	
1,2-Dichloroethane	
1,1 Dichloroethylene	
Trichloroethylene	
Tetrachloroethylene (PCE)	
Hexachlorobutadiene	
Sum of organohalogenated	
Non-carcinogenic chlorinated Aliphatic	
1,1- Dichloroethane	EPA5021 A2014- EPA 8260D2018
1,2-Dichloroethylene	
1,2-Dichloropropane	
1,1,2-Trichloroethane	
1,2,3-Trichloropropane	
1,1,2,2-Tetrachloroetane	
Pesticides	
Alachlor	EPA3546 2007 - EPA8081B 2007
Aldrin	
Atrazine	
alfa- hexachlorohexane	
beta- hexachlorohexane	
gamma- hexachlorohexane (lindane)	
Chlordane	
DDD, DDT, DDE	
Dieldrin	
Endrin	
Som of pesticides	
Other substances	
Total hydrocarbons (expressed as n-hexane)	EPA 5021 A 2014 + EPA8015 C 2007 + UNI EN ISO 9377 - 2 2002
Chlorides	
Ammoniacal nitrogen	
COD	
BOD5	
Microbiologic	
Total Coliforms	APAT CNR IRSA 7010C
Fecal Coliforms	
Fecal Streptococci	APAT CNR IRSA 7040C

Table EG07

CAROTAGGI PER ANALISI AMBIENTALI					
id SONDAGGIO	COORDINATE PUNTO		Profondità di carotaggio [m]	ANALISI SUOLI (su tre campioni) secondo il protocollo analitico di cui all'All. 5, Tit. V, P. Quarta, D.Lgs. n. 152/2006, Tabella 1. Colonna di riferimento:	Attrezzato a PIEZOMETRO per analisi acque di falda (su unico campione) secondo il protocollo analitico di cui all'All. 5, Tit. V, P. Quarta, D.Lgs. n. 152/2006, Tabella 2
	X	Y			
S1	412690.8556	4547527.542	15	A	NO
S2	412706.6706	4547474.67	15	A	NO
S3	412729.6512	4547450.264	15	A	NO
S4 (PZ-1)	412752.6318	4547393.858	25	A	SI
S5	412775.6124	4547341.452	15	A	NO
S6	412817.2514	4547305.46	15	B	NO
S7	412798.593	4547297.046	15	A	NO
S8 (PZ-2)	412843.0377	4547326.046	25	B	SI
S9	412821.3736	4547232.64	15	A	NO
S10 (PZ-3)	412910.1358	4547306.759	25	B	SI
S11 (PZ-4)	412965.439	4547236.085	25	B	SI
S12	412844.3542	4547206.234	15	A	NO
S13 (PZ-5)	412979.5846	4547272.566	25	B	SI
S14 (PZ-6)	412867.3348	4547163.828	25	A	SI
S15	412890.5154	4547115.422	15	A	NO
S16	412922.3040	4547126.46	15	B	NO
S17	413029.4657	4547192.201	15	B	NO
S18	412913.496	4547075.016	15	A	NO
S19 (PZ-7)	412943.1022	4547082.703	25	B	SI
S20 (PZ-8)	413053.3214	4547142.107	25	B	SI
S21	412936.4756	4547009.61	15	A	NO
S22 (PZ-9)	412963.9951	4546973.487	25	A	SI
S23	413012.5913	4546986.391	15	A	NO
S24 (PZ-10)	413043.3252	4547035.54	25	B	SI
S25	413058.4926	4547006.217	15	A	NO
S26	413104.3939	4547029.045	15	A	NO
S27 (PZ-11)	413150.2952	4547047.969	25	A	SI
S28	413196.3966	4547062.805	15	A	NO
S29	413244.4875	4547087.221	15	A	NO
S30	413292.5229	4547106.54	15	A	NO
S31	413277.9741	4547154.546	15	A	NO
S32	413263.2959	4547202.341	15	A	NO
S33 (PZ-12)	413248.6177	4547250.138	25	A	SI
S34	413233.9395	4547297.935	15	A	NO
S35	413219.2613	4547345.732	15	A	NO
S36	413204.5831	4547393.529	15	A	NO
S37	413189.9049	4547441.326	15	A	NO
S38 (PZ-13)	413172.7856	4547497.069	25	A	SI
S39	413155.5298	4547550.564	15	A	NO
S40	413098.9752	4547548.934	15	A	NO
S41	413041.3248	4547544.542	15	A	NO
S42	412991.3531	4547542.905	15	A	NO
S43 (PZ-14)	412941.3825	4547541.167	25	A	SI
S44	412891.4118	4547539.429	15	A	NO
S45	412841.4412	4547537.692	15	A	NO
S46	412791.4705	4547535.954	15	A	NO
S47 (PZ-15)	412741.4998	4547534.217	25	A	SI

SONDAGGI GEOTECNICI			
id SONDAGGIO	COORDINATE PUNTO		Quota sul livello del mare [m]
	X	Y	
SG-1	412940.153	4547580.203	47.99
SG-2	412879.4192	4547222.482	47.72
SG-3	413074.8016	4547088.821	46.69
SG-4	413173.1772	4547002.33	47.27

► PROFONDITA' DI PERFORAZIONE:	20 m
► NUMERO DI CAMPIONI INDISTURBATI DA PRELEVARE DA OGNI SONDAGGIO:	3

► PROTOCOLLO ANALITICO: Determinazioni geotecniche come da specifiche tecniche

TUTTE LE COORDINATE SONO ESPRESSE NEL SISTEMA DI RIFERIMENTO WGS 84/UTM zone 33N (EPSG 32633)

▦ RETICOLO A MAGLIA REGOLARE PER L'UBICAZIONE DELLE INDAGINI

◆ CAROTAGGI SEMPLICI

⧗ CAROTAGGI ATTREZZATI A PIEZOMETRO

◆ SONDAGGI PER ANALISI GEOTECNICHE

REGIONE CAMPANIA

AFFIDAMENTO DEI SERVIZI DI PROGETTAZIONE ED ESECUZIONE DEL PIANO DI CARATTERIZZAZIONE AMBIENTALE E PREDISPOSIZIONE DELL'ANALISI DI RISCHIO - INTERVENTO DI CARATTERIZZAZIONE LOTTO 2: AREA VASTA BORTOLOTTO - (Cod. PRB 1027A029)

PIANO DI CARATTERIZZAZIONE AMBIENTALE

PLANIMETRIA DI UBICAZIONE DEI SONDAGGI AMBIENTALI E GEOGNOSTICI

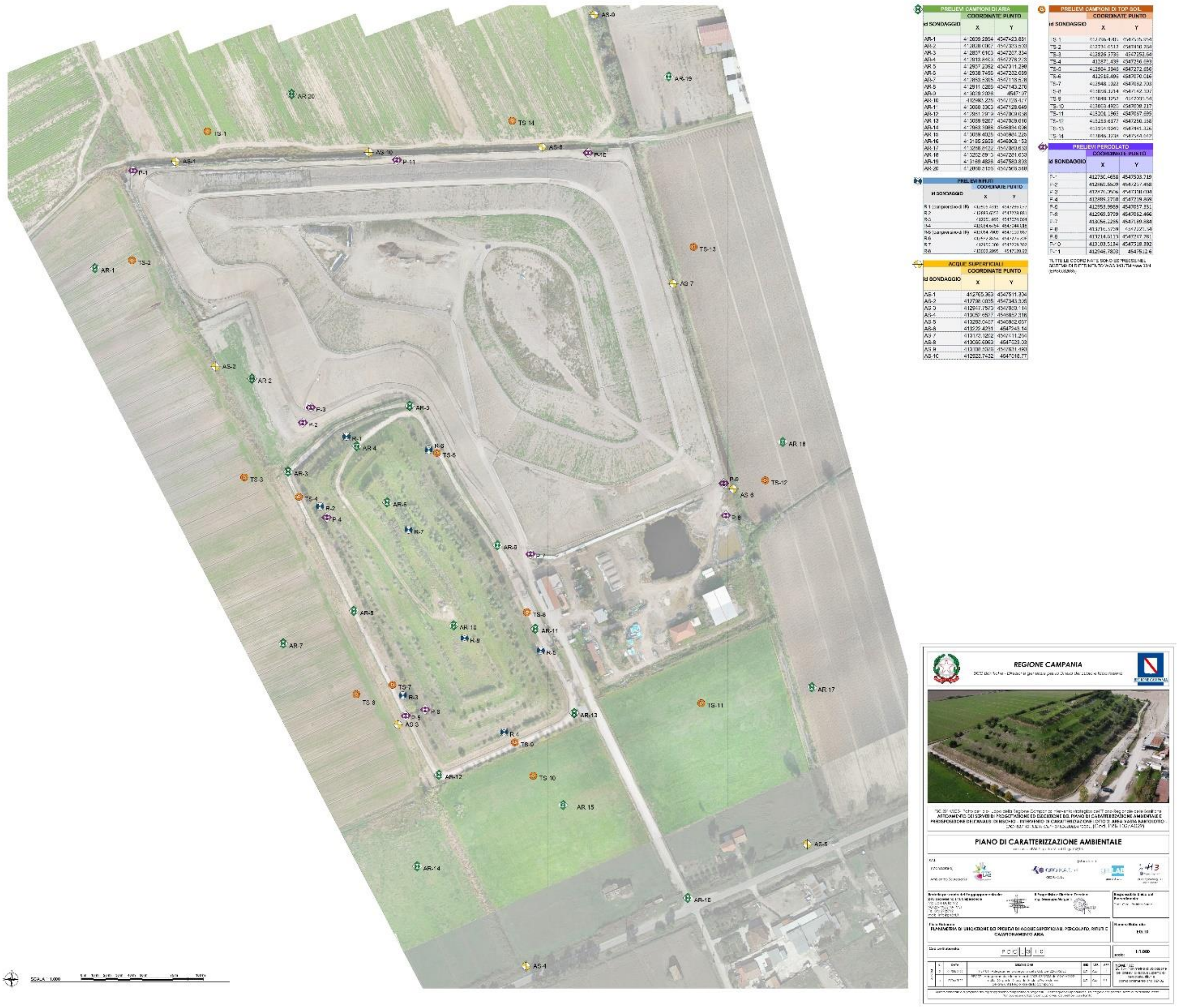
EG.07

1:1.000

Table EG09


TOMOGRAFIA 1
Lunghezza stendimento: 865 m
TOMOGRAFIA 2
Lunghezza stendimento: 780 m
TOMOGRAFIA 3
Lunghezza stendimento: 270 m
TOMOGRAFIA 4
Lunghezza stendimento: 240 m
TOMOGRAFIA 5
Lunghezza stendimento: 225 m
TOMOGRAFIA 6
Lunghezza stendimento: 200 m
TOMOGRAFIA 7
Lunghezza stendimento: 195 m
TOMOGRAFIA 8
Lunghezza stendimento: 200 m
TOMOGRAFIA 9
Lunghezza stendimento: 215 m
TOMOGRAFIA 10
Lunghezza stendimento: 295 m
TOMOGRAFIA 11
Lunghezza stendimento: 267 m
SCALA 1:500
REGIONE CAMPANIA
PIANO DI CARATTERIZZAZIONE AMBIENTALE
PLANIMETRIA DI UBICAZIONE DELLE INDAGINI GEOFISICHE
EG.09
1:500
P D C E G 0 9

Table EG10


PRELIEVI CAMPIONI DI ARIA
PRELIEVI CAMPIONI DI TOP SOIL
PRELIEVI PERCOLATO
PRELIEVI RIFIUTI
ACQUE SUPERFICIALI
COORDINATE PUNTO
Id SONDAGGIO
REGIONE CAMPANIA
PIANO DI CARATTERIZZAZIONE AMBIENTALE
SCALA 1:1000

14.2 Appendix 2: Analytical results of leachates collected in November 2021

DATA SAMPLE

Sample description:	P1
Sampling method:	*D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	**# 1200**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	3		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	1		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	14		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	29		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<0,5		5	EPA 7199 1996
*Iron	ug/l	**# 26000**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	0,2		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**# 49**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	**# 13**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	123		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**# 670**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	360		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Boron	ug/l	**# 1400**			UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*ANIONS		-			
*Nitrites	ug/l	<250		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	<200		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	23		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Naphtalene	ug/l	0,21	92		
Acenaphtylene	ug/l	0,01	97		
Acenaphtalene	ug/l	0,01	87		
Fluorene	ug/l	0,02	90		

Phenanthrene	ug/l	<0,002	94		
Anthracene	ug/l	0,004	97		
Fluoranthene	ug/l	<0,002	97		
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	
Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[e]pyrene	ug/l	<0,002			
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Dibenzo[a,l]pyrene	ug/l	<0,02			
Dibenzo[a,e]pyrene	ug/l	<0,02			
Dibenzo[a,i]pyrene	ug/l	0,03			
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenzo[a,h]anthracene	ug/l	<0,002	91	0,01	
Dibenzo[a,h]pyrene	ug/l	<0,02			
Benzo[ghi]perylene^	ug/l	<0,002	95	0,01	
Sum PAH (^)	ug/l	<0,004		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,2	90	1	
toluene	ug/l	<0,1	88	15	
Ethylbenzene	ug/l	0,1	92	50	
m-xylene p-xylene	ug/l	0,4	92	10	
o-xylene	ug/l	0,2	98		
Styrene	ug/l	<0,1	86	25	
Sum aromatic organic compound	ug/l	0,9			
*TRIHALOMETHANES		-			EPA 5021A 2014 + EPA 8260D 2018
Chloroform	ug/l	<0,1		0,15	
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	<0,2			
*VOLATILE HALOGENATED SOLVENTS		-	-		EPA 5021A 2014 + EPA 8260D 2018
*Dichlorodifluoromethane	ug/l	<0,1	-		

*Chloromethane	ug/l	<0,1	-	1,5
*Vinyl Chloride	ug/l	<0,1	-	0,5
*Bromomethane	ug/l	<0,1	-	
*Chloroethane	ug/l	<0,1	-	
*Trichlorofluoromethane	ug/l	<0,1	-	
*1,1 Dichloroethene	ug/l	<0,05	-	0,05
*Dichloromethane	ug/l	<0,1	-	
*1,2 Dichloroethene (trans)	ug/l	<0,1	-	60
*1,1 Dichloroethane	ug/l	<0,1	-	810
*1,2 Dichloroethene (cis)	ug/l	<0,1	-	60
*2,2 Dichloropropane	ug/l	<0,1	-	
*Bromochloromethane	ug/l	<0,1	-	
*1,1,1 Trichlorethane	ug/l	<0,1	-	
*1,1 Dichloropropene	ug/l	<0,1	-	
*Carbon tetrachloride	ug/l	<0,1	-	
*1,2 Dichloroethane	ug/l	<0,1	-	3
*1,2 Dichloropropane	ug/l	<0,1	-	0,15
*Dibromomethane	ug/l	<0,1	-	
*cis 1,3 Dichloropropene	ug/l	<0,1	-	
*trans 1,3 Dichloropropene	ug/l	<0,1	-	
*1,1,2 Trichlorethane	ug/l	<0,1	-	0,2
*1,3 Dichloropropane	ug/l	<0,1	-	
*Chlorobenzene	ug/l	0,1	-	40
*1,1,1,2 Tetrachloroethane	ug/l	<0,1	-	
*Isopropylbenzene	ug/l	0,7	-	
*bromobenzene	ug/l	<0,1	-	
*n-Propylbenzene	ug/l	<0,1	-	
*2 Chlorotoluene	ug/l	<0,1	-	
*1,3,5 Trimethylbenzene	ug/l	<0,1	-	
*1,2,4 Trimethylbenzene	ug/l	<0,1	-	
*4 Chlorotoluene	ug/l	<0,1	-	
*sec-Butylbenzene	ug/l	<0,1	-	
*1,3 Dichlorobenzene	ug/l	0,1	-	
*tert-Butylbenzene	ug/l	<0,1	-	

*p-Isopropyltoluene	ug/l	0,3	-		
*1,4 Dichlorobenzene	ug/l	0,2	-	0,5	
*n-butylbenzene	ug/l	<0,1	-		
*1,2 Dichlorobenzene	ug/l	<0,1	-	270	
*1,2 Dibromo-3-chloropropane	ug/l	<0,1	-		
*1,2,4 Trichlorobenzene	ug/l	<0,1	-	190	
*Hexachlorobutadiene	ug/l	<0,1	-	0,15	
*Naphthalene	ug/l	<0,1	-		
*1,2,3 Trichlorobenzene	ug/l	<0,1	-		
*SOMMATORIA Trichlorethene e Tetrachlorethene	ug/l	<0,1	-		EPA 5021A 2014 + EPA 8260D 2018
*Trichlorethene	ug/l	<0,1	-	1,5	
*Tetrachlorethene	ug/l	<0,1	-	1,1	
*NITROBENZENS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Nitrobenzene	ug/l	0,03	-	3,5	
*1,2-Dinitrobenzene	ug/l	0,03	-	15	
*1,3-Dinitrobenzene	ug/l	0,03	-	3,7	
*1-chloro-2-nitrobenzene	ug/l	<0,02	-		
*1-chloro-3-nitrobenzene	ug/l	<0,02	-		
*1-chloro-4-nitrobenzene	ug/l	<0,02	-		
*Chloronitrobenzens (each one)	ug/l	<0,03	-	0,5	
* SEMIVOLATILE CHLOROBENZENES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Pentachloroethane	ug/l	<0,02	-		
*Hexachloroethane	ug/l	<0,02	-		
*1,2,4-trichlorobenzene	ug/l	0,32	-	190	
*Hexachloropropene	ug/l	<0,02	-		
*Hexachlorobutadiene	ug/l	<0,02	-		
*Hexachlorociclopentadiene	ug/l	<0,02	-		
*1,2,4,5-tetrachlorobenzene	ug/l	<0,02	-	1,8	
*2-chloronaphtalene	ug/l	<0,02	-		
*Pentachlorobenzene	ug/l	<0,02	-	5	
*Hexachlorobenzene	ug/l	<0,002	-	0,01	
*PHENOLS AND CHLOROPHENOLS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*2-Chlorophenol	ug/l	<0,02	-	180	
*2,4-Dichlorophenol	ug/l	<0,02	-	110	

*2,4,6-Trichlorophrnol	ug/l	<0,02	-	5	
*Pentachlorophenol	ug/l	<0,02	-	0,5	
*AROMATIC AMINES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Aniline	ug/l	<0,02	-	10	
* diphenylamine	ug/l	<0,02	-	910	
*o,p-Toluidine	ug/l	<0,02	-	0,35	
* ORGANOCHLORINATED PESTICIDES		-	-		EPA 3510C 1996 + EPA 8081 B 2007
*pentachlorobenzene	ug/l	<0,0001	-		
*Alpha- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Hexachlorobenzene	ug/l	<0,0001	-		
*Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Delta- hexachlorohexane	ug/l	<0,0001	-		
*Eptachlor	ug/l	<0,0001	-		
*Aldrin	ug/l	<0,0001	-	0,03	
*Atrazine	ug/l	<0,0001	-	0,3	
*Alaclor	ug/l	<0,0001	-	0,1	
*Isodrin	ug/l	<0,0001	-		
*Eptaclor Epossid	ug/l	<0,0001	-		
*Endosulfan I	ug/l	<0,0001	-		
*Alpha Chlordane	ug/l	<0,0001	-		
*Gamma Chlordane	ug/l	<0,0001	-		
*Dieldrin	ug/l	<0,0001	-	0,1	
*4-4'-DDE	ug/l	<0,0001	-		
*Endrin	ug/l	<0,0001	-	0,1	
*2,4_DDD	ug/l	<0,0001	-		
*2,4_DDE	ug/l	<0,0001	-		
*2,4-DDT	ug/l	<0,0001	-		
*Endosulfan II	ug/l	<0,0001	-		
*4-4'-DDD	ug/l	<0,0001	-		
*4-4'-DDT	ug/l	<0,0001	-		
* Methoxychlor	ug/l	<0,0001	-		
*Chlordane	ug/l	<0,0001	-	0,1	
*DDD, DDT, DDE	ug/l	<0,0001	-	0,1	
*Sum organochlorinated pesticides	ug/l	<0,001	-	0,5	
**POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-	-		EPA 3510C 1996 + EPA 8082A 2007

*2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		
*2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
*2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
*2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
*2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
*2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
*2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
*2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
*3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
*3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
*2,2',3,5,5',6-HxCB (PCB-151)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-118+149)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
*2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
*2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
*2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
*2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
*2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
*3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
*2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
*2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
*2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
*2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
*2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
*2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
*2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
*3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
*2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
*2,3,3',4,4',5,5'-HpCB (PCB-189)	ug/l	<0,0004	-		
* Sum Polichlorobiphenils (PCB)	ug/l	<0,007	-	0,01	
Total Hydrocarbons (expressed as n-hexane	ug/l	120	95	350	UNI EN ISO 9377-2:2002
* DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001	-		EPA 3546 2007+ EPA 8280B 2007

DATA SAMPLE

Sample description: P3

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	**# 390**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	1,4		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	**# 40**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	0,7		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	21		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	35		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<0,5		5	EPA 7199 1996
*Iron	ug/l	**# 8900**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	<0,1		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**# 26**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	8		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	5,4		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**# 2400**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	37		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Boron	ug/l	**# 1600**			UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*ANIONS		-			
*Nitrites	ug/l	<100		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	730		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	27		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Naphtalene	ug/l	0,3	92		
Acenaphtylene	ug/l	0,006	97		
Acenaphtalene	ug/l	0,02	87		
Fluorene	ug/l	0,01	90		

Phenanthrene	ug/l	0,009	94		
Anthracene	ug/l	0,004	97		
Fluoranthene	ug/l	<0,002	97		
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	
Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[e]pyrene	ug/l	<0,002			
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Dibenzo[a,l]pyrene	ug/l	<0,02			
Dibenzo[a,e]pyrene	ug/l	<0,02			
Dibenzo[a,i]pyrene	ug/l	<0,02			
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenzo[a,h]anthracene	ug/l	<0,002	91	0,01	
Dibenzo[a,h]pyrene	ug/l	<0,02			
Benzo[ghi]perylene^	ug/l	<0,002	95	0,01	
Sum PAH (^)	ug/l	<0,004		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,75	90	1	
toluene	ug/l	0,2	88	15	
Ethylbenzene	ug/l	0,3	92	50	
m-xylene p-xylene	ug/l	1	92	10	
o-xylene	ug/l	0,4	98		
Styrene	ug/l	0,2	86	25	
Sum aromatic organic compound	ug/l	3			
*TRIHALOMETHANES		-			EPA 5021A 2014 + EPA 8260D 2018
Chloroform	ug/l	<0,1		0,15	
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	<0,2			
*VOLATILE HALOGENATED SOLVENTS		-	-		EPA 5021A 2014 + EPA 8260D 2018
*Dichlorodifluoromethane	ug/l	0,2	-		

*Chloromethane	ug/l	<0,1	-	1,5
*Vinyl Chloride	ug/l	<0,1	-	0,5
*Bromomethane	ug/l	<0,1	-	
*Chloroethane	ug/l	<0,1	-	
*Trichlorofluoromethane	ug/l	<0,1	-	
*1,1 Dichloroethene	ug/l	<0,05	-	0,05
*Dichloromethane	ug/l	<0,1	-	
*1,2 Dichloroethene (trans)	ug/l	<0,1	-	60
*1,1 Dichloroethane	ug/l	<0,1	-	810
*1,2 Dichloroethene (cis)	ug/l	0,2	-	60
*2,2 Dichloropropane	ug/l	<0,1	-	
*Bromochloromethane	ug/l	<0,1	-	
*1,1,1 Trichlorethane	ug/l	<0,1	-	
*1,1 Dichloropropene	ug/l	<0,1	-	
*Carbon tetrachloride	ug/l	<0,1	-	
*1,2 Dichloroethane	ug/l	<0,1	-	3
*1,2 Dichloropropane	ug/l	<0,1	-	0,15
*Dibromomethane	ug/l	<0,1	-	
*cis 1,3 Dichloropropene	ug/l	<0,1	-	
*trans 1,3 Dichloropropene	ug/l	<0,1	-	
*1,1,2 Trichlorethane	ug/l	<0,1	-	0,2
*1,3 Dichloropropane	ug/l	<0,1	-	
*Chlorobenzene	ug/l	0,4	-	40
*1,1,1,2 Tetrachloroethane	ug/l	<0,1	-	
*Isopropylbenzene	ug/l	0,2	-	
*bromobenzene	ug/l	<0,1	-	
*n-Propylbenzene	ug/l	0,1	-	
*2 Chlorotoluene	ug/l	<0,1	-	
*1,3,5 Trimethylbenzene	ug/l	<0,1	-	
*1,2,4 Trimethylbenzene	ug/l	0,2	-	
*4 Chlorotoluene	ug/l	<0,1	-	
*sec-Butylbenzene	ug/l	<0,1	-	
*1,3 Dichlorobenzene	ug/l	<0,1	-	
*tert-Butylbenzene	ug/l	<0,1	-	

*p-Isopropyltoluene	ug/l	1	-		
*1,4 Dichlorobenzene	ug/l	0,2	-	0,5	
*n-butylbenzene	ug/l	<0,1	-		
*1,2 Dichlorobenzene	ug/l	<0,1	-	270	
*1,2 Dibromo-3-chloropropane	ug/l	<0,1	-		
*1,2,4 Trichlorobenzene	ug/l	<0,1	-	190	
*Hexachlorobutadiene	ug/l	<0,1	-	0,15	
*Naphthalene	ug/l	1	-		
*1,2,3 Trichlorobenzene	ug/l	<0,1	-		
*SOMMATORIA Trichlorethene e Tetrachlorethene	ug/l	<0,1	-		EPA 5021A 2014 + EPA 8260D 2018
*Trichlorethene	ug/l	<0,1	-	1,5	
*Tetrachlorethene	ug/l	<0,1	-	1,1	
*NITROBENZENS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Nitrobenzene	ug/l	<0,02	-	3,5	
*1,2-Dinitrobenzene	ug/l	<0,02	-	15	
*1,3-Dinitrobenzene	ug/l	<0,02	-	3,7	
*1-chloro-2-nitrobenzene	ug/l	<0,02	-		
*1-chloro-3-nitrobenzene	ug/l	<0,02	-		
*1-chloro-4-nitrobenzene	ug/l	<0,02	-		
*Chloronitrobenzens (each one)	ug/l	<0,03	-	0,5	
* SEMIVOLATILE CHLOROBENZENES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Pentachloroethane	ug/l	<0,02	-		
*Hexachloroethane	ug/l	<0,02	-		
*1,2,4-trichlorobenzene	ug/l	<0,02	-	190	
*Hexachloropropene	ug/l	<0,02	-		
*Hexachlorobutadiene	ug/l	<0,02	-		
*Hexachlorociclopentadiene	ug/l	<0,02	-		
*1,2,4,5-tetrachlorobenzene	ug/l	<0,02	-	1,8	
*2-chloronaphtalene	ug/l	<0,02	-		
*Pentachlorobenzene	ug/l	<0,02	-	5	
*Hexachlorobenzene	ug/l	<0,002	-	0,01	
*PHENOLS AND CHLOROPHENOLS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*2-Chlorophenol	ug/l	<0,02	-	180	
*2,4-Dichlorophenol	ug/l	<0,02	-	110	

*2,4,6-Trichlorophrnol	ug/l	<0,02	-	5	
*Pentachlorophenol	ug/l	<0,02	-	0,5	
*AROMATIC AMINES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Aniline	ug/l	<0,02	-	10	
* diphenylamine	ug/l	0,04	-	910	
*o,p-Toluidine	ug/l	<0,02	-	0,35	
* ORGANOCHLORINATED PESTICIDES		-	-		EPA 3510C 1996 + EPA 8081 B 2007
*pentachlorobenzene	ug/l	<0,0001	-		
*Alpha- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Hexachlorobenzene	ug/l	<0,0001	-		
*Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Delta- hexachlorohexane	ug/l	<0,0001	-		
*Eptachlor	ug/l	<0,0001	-		
*Aldrin	ug/l	<0,0001	-	0,03	
*Atrazine	ug/l	<0,0001	-	0,3	
*Alaclor	ug/l	<0,0001	-	0,1	
*Isodrin	ug/l	<0,0001	-		
*Eptaclor Epossid	ug/l	<0,0001	-		
*Endosulfan I	ug/l	<0,0001	-		
*Alpha Chlordane	ug/l	<0,0001	-		
*Gamma Chlordane	ug/l	<0,0001	-		
*Dieldrin	ug/l	<0,0001	-	0,1	
*4-4'-DDE	ug/l	<0,0001	-		
*Endrin	ug/l	<0,0001	-	0,1	
*2,4_DDD	ug/l	<0,0001	-		
*2,4_DDE	ug/l	<0,0001	-		
*2,4-DDT	ug/l	<0,0001	-		
*Endosulfan II	ug/l	<0,0001	-		
*4-4'-DDD	ug/l	<0,0001	-		
*4-4'-DDT	ug/l	<0,0001	-		
* Methoxychlor	ug/l	<0,0001	-		
*Chlordane	ug/l	<0,0001	-	0,1	
*DDD, DDT, DDE	ug/l	<0,0001	-	0,1	
*Sum organochlorinated pesticides	ug/l	<0,001	-	0,5	
**POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-	-		EPA 3510C 1996 + EPA 8082A 2007

*2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		
*2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
*2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
*2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
*2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
*2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
*2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
*2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
*3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
*3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
*2,2',3,5,5',6-HxCB (PCB-151)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-118+149)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
*2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
*2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
*2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
*2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
*2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
*3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
*2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
*2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
*2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
*2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
*2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
*2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
*2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
*3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
*2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
*2,3,3',4,4',5,5'-HpCB (PCB-189)	ug/l	<0,0004	-		
* Sum Polichlorobiphenils (PCB)	ug/l	<0,007	-	0,01	
Total Hydrocarbons (expressed as n-hexane	ug/l	300	95	350	UNI EN ISO 9377-2:2002
* DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001	-		EPA 3546 2007+ EPA 8280B 2007

DATA SAMPLE

Sample description: P4

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	13		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	1,1		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	1,8		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	3,6		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	16		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<0,5		5	EPA 7199 1996
*Iron	ug/l	**# 2300**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	<0,1		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	6,4		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	0,7		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**# 930**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	4,8		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Boron	ug/l	580			UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*ANIONS		-			
*Nitrites	ug/l	<250		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	250		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	**# 350**		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Naphtalene	ug/l	0,12	92		
Acenaphtylene	ug/l	0,01	97		
Acenaphtalene	ug/l	0,01	87		
Fluorene	ug/l	0,02	90		

Phenanthrene	ug/l	0,005	94		
Anthracene	ug/l	0,005	97		
Fluoranthene	ug/l	0,002	97		
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	
Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[e]pyrene	ug/l	<0,002			
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Dibenzo[a,l]pyrene	ug/l	<0,02			
Dibenzo[a,e]pyrene	ug/l	<0,02			
Dibenzo[a,i]pyrene	ug/l	<0,02			
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenzo[a,h]anthracene	ug/l	<0,002	91	0,01	
Dibenzo[a,h]pyrene	ug/l	<0,02			
Benzo[ghi]perylene^	ug/l	<0,002	95	0,01	
Sum PAH (^)	ug/l	<0,004		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,5	90	1	
toluene	ug/l	2	88	15	
Ethylbenzene	ug/l	2	92	50	
m-xylene p-xylene	ug/l	4	92	10	
o-xylene	ug/l	1	98		
Styrene	ug/l	0,3	86	25	
Sum aromatic organic compound	ug/l	10			
*TRIHALOMETHANES		-			EPA 5021A 2014 + EPA 8260D 2018
Chloroform	ug/l	<0,1		0,15	
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	<0,2			
*VOLATILE HALOGENATED SOLVENTS		-	-		EPA 5021A 2014 + EPA 8260D 2018
*Dichlorodifluoromethane	ug/l	0,3	-		

*Chloromethane	ug/l	<0,1	-	1,5
*Vinyl Chloride	ug/l	0,4	-	0,5
*Bromomethane	ug/l	<0,1	-	
*Chloroethane	ug/l	<0,1	-	
*Trichlorofluoromethane	ug/l	<0,1	-	
*1,1 Dichloroethene	ug/l	<0,05	-	0,05
*Dichloromethane	ug/l	<0,1	-	
*1,2 Dichloroethene (trans)	ug/l	<0,1	-	60
*1,1 Dichloroethane	ug/l	<0,1	-	810
*1,2 Dichloroethene (cis)	ug/l	0,2	-	60
*2,2 Dichloropropane	ug/l	<0,1	-	
*Bromochloromethane	ug/l	<0,1	-	
*1,1,1 Trichlorethane	ug/l	<0,1	-	
*1,1 Dichloropropene	ug/l	<0,1	-	
*Carbon tetrachloride	ug/l	<0,1	-	
*1,2 Dichloroethane	ug/l	<0,1	-	3
*1,2 Dichloropropane	ug/l	<0,1	-	0,15
*Dibromomethane	ug/l	<0,1	-	
*cis 1,3 Dichloropropene	ug/l	<0,1	-	
*trans 1,3 Dichloropropene	ug/l	<0,1	-	
*1,1,2 Trichlorethane	ug/l	<0,1	-	0,2
*1,3 Dichloropropane	ug/l	<0,1	-	
*Chlorobenzene	ug/l	<0,1	-	40
*1,1,1,2 Tetrachloroethane	ug/l	<0,1	-	
*Isopropylbenzene	ug/l	0,6	-	
*bromobenzene	ug/l	<0,1	-	
*n-Propylbenzene	ug/l	0,6	-	
*2 Chlorotoluene	ug/l	<0,1	-	
*1,3,5 Trimethylbenzene	ug/l	0,5	-	
*1,2,4 Trimethylbenzene	ug/l	2	-	
*4 Chlorotoluene	ug/l	<0,1	-	
*sec-Butylbenzene	ug/l	<0,1	-	
*1,3 Dichlorobenzene	ug/l	<0,1	-	
*tert-Butylbenzene	ug/l	<0,1	-	

*p-Isopropyltoluene	ug/l	41	-		
*1,4 Dichlorobenzene	ug/l	0,4	-	0,5	
*n-butylbenzene	ug/l	<0,1	-		
*1,2 Dichlorobenzene	ug/l	<0,1	-	270	
*1,2 Dibromo-3-chloropropane	ug/l	<0,1	-		
*1,2,4 Trichlorobenzene	ug/l	<0,1	-	190	
*Hexachlorobutadiene	ug/l	<0,1	-	0,15	
*Naphthalene	ug/l	3	-		
*1,2,3 Trichlorobenzene	ug/l	<0,1	-		
*SOMMATORIA Trichlorethene e Tetrachlorethene	ug/l	<0,1	-		EPA 5021A 2014 + EPA 8260D 2018
*Trichlorethene	ug/l	<0,1	-	1,5	
*Tetrachlorethene	ug/l	<0,1	-	1,1	
*NITROBENZENS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Nitrobenzene	ug/l	<0,02	-	3,5	
*1,2-Dinitrobenzene	ug/l	<0,02	-	15	
*1,3-Dinitrobenzene	ug/l	<0,02	-	3,7	
*1-chloro-2-nitrobenzene	ug/l	<0,02	-		
*1-chloro-3-nitrobenzene	ug/l	<0,02	-		
*1-chloro-4-nitrobenzene	ug/l	<0,02	-		
*Chloronitrobenzens (each one)	ug/l	<0,03	-	0,5	
* SEMIVOLATILE CHLOROBENZENES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Pentachloroethane	ug/l	<0,02	-		
*Hexachloroethane	ug/l	<0,02	-		
*1,2,4-trichlorobenzene	ug/l	<0,02	-	190	
*Hexachloropropene	ug/l	<0,02	-		
*Hexachlorobutadiene	ug/l	<0,02	-		
*Hexachlorociclopentadiene	ug/l	<0,02	-		
*1,2,4,5-tetrachlorobenzene	ug/l	<0,02	-	1,8	
*2-chloronaphtalene	ug/l	<0,02	-		
*Pentachlorobenzene	ug/l	<0,02	-	5	
*Hexachlorobenzene	ug/l	<0,002	-	0,01	
*PHENOLS AND CHLOROPHENOLS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*2-Chlorophenol	ug/l	<0,02	-	180	
*2,4-Dichlorophenol	ug/l	<0,02	-	110	

*2,4,6-Trichlorophrnol	ug/l	<0,02	-	5	
*Pentachlorophenol	ug/l	<0,02	-	0,5	
*AROMATIC AMINES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Aniline	ug/l	<0,02	-	10	
* diphenylamine	ug/l	0,07	-	910	
*o,p-Toluidine	ug/l	<0,02	-	0,35	
* ORGANOCHLORINATED PESTICIDES		-	-		EPA 3510C 1996 + EPA 8081 B 2007
*pentachlorobenzene	ug/l	<0,0001	-		
*Alpha- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Hexachlorobenzene	ug/l	<0,0001	-		
*Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Delta- hexachlorohexane	ug/l	<0,0001	-		
*Eptachlor	ug/l	<0,0001	-		
*Aldrin	ug/l	<0,0001	-	0,03	
*Atrazine	ug/l	<0,0001	-	0,3	
*Alaclor	ug/l	<0,0001	-	0,1	
*Isodrin	ug/l	<0,0001	-		
*Eptaclor Epossid	ug/l	<0,0001	-		
*Endosulfan I	ug/l	<0,0001	-		
*Alpha Chlordane	ug/l	<0,0001	-		
*Gamma Chlordane	ug/l	<0,0001	-		
*Dieldrin	ug/l	<0,0001	-	0,1	
*4-4'-DDE	ug/l	<0,0001	-		
*Endrin	ug/l	<0,0001	-	0,1	
*2,4_DDD	ug/l	<0,0001	-		
*2,4_DDE	ug/l	<0,0001	-		
*2,4-DDT	ug/l	<0,0001	-		
*Endosulfan II	ug/l	<0,0001	-		
*4-4'-DDD	ug/l	<0,0001	-		
*4-4'-DDT	ug/l	<0,0001	-		
* Methoxychlor	ug/l	<0,0001	-		
*Chlordane	ug/l	<0,0001	-	0,1	
*DDD, DDT, DDE	ug/l	<0,0001	-	0,1	
*Sum organochlorinated pesticides	ug/l	<0,001	-	0,5	
**POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-	-		EPA 3510C 1996 + EPA 8082A 2007

*2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		
*2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
*2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
*2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
*2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
*2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
*2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
*2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
*3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
*3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
*2,2',3,5,5',6-HxCB (PCB-151)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-118+149)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
*2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
*2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
*2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
*2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
*2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
*3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
*2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
*2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
*2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
*2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
*2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
*2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
*2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
*3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
*2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
*2,3,3',4,4',5,5'-HpCB (PCB-189)	ug/l	<0,0004	-		
* Sum Polichlorobiphenils (PCB)	ug/l	<0,007	-	0,01	
Total Hydrocarbons (expressed as n-hexane	ug/l	210	95	350	UNI EN ISO 9377-2:2002
* DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001	-		EPA 3546 2007+ EPA 8280B 2007

DATA SAMPLE

Sample description: P5

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	56		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	2		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	4		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	6		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	**# 53**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<0,5		5	EPA 7199 1996
*Iron	ug/l	**# 10800**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	<0,1		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	11		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	1		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	1		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**# 360**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	11		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Boron	ug/l	920			UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*ANIONS		-			
*Nitrites	ug/l	<250		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	<200		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	52		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Naphtalene	ug/l	0,3	92		
Acenaphtylene	ug/l	0,006	97		
Acenaphtalene	ug/l	0,02	87		
Fluorene	ug/l	0,01	90		

Phenanthrene	ug/l	0,009	94		
Anthracene	ug/l	0,004	97		
Fluoranthene	ug/l	<0,002	97		
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	
Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[e]pyrene	ug/l	<0,002			
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Dibenzo[a,l]pyrene	ug/l	<0,02			
Dibenzo[a,e]pyrene	ug/l	<0,02			
Dibenzo[a,i]pyrene	ug/l	<0,02			
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenzo[a,h]anthracene	ug/l	<0,002	91	0,01	
Dibenzo[a,h]pyrene	ug/l	<0,02			
Benzo[ghi]perylene^	ug/l	<0,002	95	0,01	
Sum PAH (^)	ug/l	<0,004		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,97	90	1	
toluene	ug/l	3	88	15	
Ethylbenzene	ug/l	3	92	50	
m-xylene p-xylene	ug/l	6	92	10	
o-xylene	ug/l	2	98		
Styrene	ug/l	0,4	86	25	
Sum aromatic organic compound	ug/l	15			
*TRIHALOMETHANES		-			EPA 5021A 2014 + EPA 8260D 2018
Chloroform	ug/l	<0,1		0,15	
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	<0,2			
*VOLATILE HALOGENATED SOLVENTS		-	-		EPA 5021A 2014 + EPA 8260D 2018
*Dichlorodifluoromethane	ug/l	0,5	-		

*Chloromethane	ug/l	<0,1	-	1,5
*Vinyl Chloride	ug/l	<0,1	-	0,5
*Bromomethane	ug/l	<0,1	-	
*Chloroethane	ug/l	<0,1	-	
*Trichlorofluoromethane	ug/l	<0,1	-	
*1,1 Dichloroethene	ug/l	<0,05	-	0,05
*Dichloromethane	ug/l	<0,1	-	
*1,2 Dichloroethene (trans)	ug/l	<0,1	-	60
*1,1 Dichloroethane	ug/l	<0,1	-	810
*1,2 Dichloroethene (cis)	ug/l	0,1	-	60
*2,2 Dichloropropane	ug/l	<0,1	-	
*Bromochloromethane	ug/l	<0,1	-	
*1,1,1 Trichlorethane	ug/l	<0,1	-	
*1,1 Dichloropropene	ug/l	<0,1	-	
*Carbon tetrachloride	ug/l	<0,1	-	
*1,2 Dichloroethane	ug/l	<0,1	-	3
*1,2 Dichloropropane	ug/l	<0,1	-	0,15
*Dibromomethane	ug/l	<0,1	-	
*cis 1,3 Dichloropropene	ug/l	<0,1	-	
*trans 1,3 Dichloropropene	ug/l	<0,1	-	
*1,1,2 Trichlorethane	ug/l	<0,1	-	0,2
*1,3 Dichloropropane	ug/l	<0,1	-	
*Chlorobenzene	ug/l	<0,1	-	40
*1,1,1,2 Tetrachloroethane	ug/l	<0,1	-	
*Isopropylbenzene	ug/l	0,6	-	
*bromobenzene	ug/l	<0,1	-	
*n-Propylbenzene	ug/l	0,6	-	
*2 Chlorotoluene	ug/l	<0,1	-	
*1,3,5 Trimethylbenzene	ug/l	0,7	-	
*1,2,4 Trimethylbenzene	ug/l	3	-	
*4 Chlorotoluene	ug/l	<0,1	-	
*sec-Butylbenzene	ug/l	<0,1	-	
*1,3 Dichlorobenzene	ug/l	<0,1	-	
*tert-Butylbenzene	ug/l	<0,1	-	

*p-Isopropyltoluene	ug/l	36	-		
*1,4 Dichlorobenzene	ug/l	0,2	-	0,5	
*n-butylbenzene	ug/l	<0,1	-		
*1,2 Dichlorobenzene	ug/l	<0,1	-	270	
*1,2 Dibromo-3-chloropropane	ug/l	<0,1	-		
*1,2,4 Trichlorobenzene	ug/l	<0,1	-	190	
*Hexachlorobutadiene	ug/l	<0,1	-	0,15	
*Naphthalene	ug/l	5	-		
*1,2,3 Trichlorobenzene	ug/l	<0,1	-		
*SOMMATORIA Trichlorethene e Tetrachlorethene	ug/l	<0,1	-		EPA 5021A 2014 + EPA 8260D 2018
*Trichlorethene	ug/l	<0,1	-	1,5	
*Tetrachlorethene	ug/l	<0,1	-	1,1	
*NITROBENZENS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Nitrobenzene	ug/l	<0,02	-	3,5	
*1,2-Dinitrobenzene	ug/l	<0,02	-	15	
*1,3-Dinitrobenzene	ug/l	<0,02	-	3,7	
*1-chloro-2-nitrobenzene	ug/l	<0,02	-		
*1-chloro-3-nitrobenzene	ug/l	<0,02	-		
*1-chloro-4-nitrobenzene	ug/l	<0,02	-		
*Chloronitrobenzens (each one)	ug/l	<0,03	-	0,5	
* SEMIVOLATILE CHLOROBENZENES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Pentachloroethane	ug/l	<0,02	-		
*Hexachloroethane	ug/l	<0,02	-		
*1,2,4-trichlorobenzene	ug/l	<0,02	-	190	
*Hexachloropropene	ug/l	<0,02	-		
*Hexachlorobutadiene	ug/l	<0,02	-		
*Hexachlorociclopentadiene	ug/l	<0,02	-		
*1,2,4,5-tetrachlorobenzene	ug/l	<0,02	-	1,8	
*2-chloronaphtalene	ug/l	<0,02	-		
*Pentachlorobenzene	ug/l	<0,02	-	5	
*Hexachlorobenzene	ug/l	<0,002	-	0,01	
*PHENOLS AND CHLOROPHENOLS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*2-Chlorophenol	ug/l	<0,02	-	180	
*2,4-Dichlorophenol	ug/l	<0,02	-	110	

*2,4,6-Trichlorophrnol	ug/l	<0,02	-	5	
*Pentachlorophenol	ug/l	<0,02	-	0,5	
*AROMATIC AMINES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Aniline	ug/l	<0,02	-	10	
* diphenylamine	ug/l	0,04	-	910	
*o,p-Toluidine	ug/l	<0,02	-	0,35	
* ORGANOCHLORINATED PESTICIDES		-	-		EPA 3510C 1996 + EPA 8081 B 2007
*pentachlorobenzene	ug/l	<0,0001	-		
*Alpha- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Hexachlorobenzene	ug/l	<0,0001	-		
*Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Delta- hexachlorohexane	ug/l	<0,0001	-		
*Eptachlor	ug/l	<0,0001	-		
*Aldrin	ug/l	<0,0001	-	0,03	
*Atrazine	ug/l	<0,0001	-	0,3	
*Alaclor	ug/l	<0,0001	-	0,1	
*Isodrin	ug/l	<0,0001	-		
*Eptaclor Epossid	ug/l	<0,0001	-		
*Endosulfan I	ug/l	<0,0001	-		
*Alpha Chlordane	ug/l	<0,0001	-		
*Gamma Chlordane	ug/l	<0,0001	-		
*Dieldrin	ug/l	<0,0001	-	0,1	
*4-4'-DDE	ug/l	<0,0001	-		
*Endrin	ug/l	<0,0001	-	0,1	
*2,4_DDD	ug/l	<0,0001	-		
*2,4_DDE	ug/l	<0,0001	-		
*2,4-DDT	ug/l	<0,0001	-		
*Endosulfan II	ug/l	<0,0001	-		
*4-4'-DDD	ug/l	<0,0001	-		
*4-4'-DDT	ug/l	<0,0001	-		
* Methoxychlor	ug/l	<0,0001	-		
*Chlordane	ug/l	<0,0001	-	0,1	
*DDD, DDT, DDE	ug/l	<0,0001	-	0,1	
*Sum organochlorinated pesticides	ug/l	<0,001	-	0,5	
**POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-	-		EPA 3510C 1996 + EPA 8082A 2007

*2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		
*2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
*2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
*2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
*2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
*2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
*2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
*2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
*3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
*3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
*2,2',3,5,5',6-HxCB (PCB-151)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-118+149)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
*2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
*2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
*2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
*2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
*2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
*3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
*2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
*2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
*2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
*2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
*2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
*2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
*2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
*3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
*2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
*2,3,3',4,4',5,5'-HpCB (PCB-189)	ug/l	<0,0004	-		
* Sum Polichlorobiphenils (PCB)	ug/l	<0,007	-	0,01	
Total Hydrocarbons (expressed as n-hexane	ug/l	220	95	350	UNI EN ISO 9377-2:2002
* DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001	-		EPA 3546 2007+ EPA 8280B 2007

DATA SAMPLE

Sample description: P6

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	62		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	2,4		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	5,8		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	0,8		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	10		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	18		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<0,5		5	EPA 7199 1996
*Iron	ug/l	**# 620**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	<0,1		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	16		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	5,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	43		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**# 830**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	73		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Boron	ug/l	**# 1100**			UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*ANIONS		-			
*Nitrites	ug/l	250		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	420		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	28		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Naphtalene	ug/l	0,01	92		
Acenaphtylene	ug/l	0,005	97		
Acenaphtalene	ug/l	0,004	87		
Fluorene	ug/l	0,01	90		

Phenanthrene	ug/l	<0,002	94		
Anthracene	ug/l	0,002	97		
Fluoranthene	ug/l	<0,002	97		
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	
Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[e]pyrene	ug/l	<0,002			
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Dibenzo[a,l]pyrene	ug/l	<0,02			
Dibenzo[a,e]pyrene	ug/l	<0,02			
Dibenzo[a,i]pyrene	ug/l	0,03			
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenzo[a,h]anthracene	ug/l	<0,002	91	0,01	
Dibenzo[a,h]pyrene	ug/l	<0,02			
Benzo[ghi]perylene^	ug/l	<0,002	95	0,01	
Sum PAH (^)	ug/l	<0,004		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,2	90	1	
toluene	ug/l	<0,1	88	15	
Ethylbenzene	ug/l	<0,1	92	50	
m-xylene p-xylene	ug/l	0,2	92	10	
o-xylene	ug/l	<0,1	98		
Styrene	ug/l	<0,1	86	25	
Sum aromatic organic compound	ug/l	0,4			
*TRIHALOMETHANES		-			EPA 5021A 2014 + EPA 8260D 2018
Chloroform	ug/l	<0,1		0,15	
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	<0,2			
*VOLATILE HALOGENATED SOLVENTS		-	-		EPA 5021A 2014 + EPA 8260D 2018
*Dichlorodifluoromethane	ug/l	<0,1	-		

*Chloromethane	ug/l	<0,1	-	1,5
*Vinyl Chloride	ug/l	<0,1	-	0,5
*Bromomethane	ug/l	<0,1	-	
*Chloroethane	ug/l	<0,1	-	
*Trichlorofluoromethane	ug/l	<0,1	-	
*1,1 Dichloroethene	ug/l	<0,05	-	0,05
*Dichloromethane	ug/l	<0,1	-	
*1,2 Dichloroethene (trans)	ug/l	<0,1	-	60
*1,1 Dichloroethane	ug/l	<0,1	-	810
*1,2 Dichloroethene (cis)	ug/l	<0,1	-	60
*2,2 Dichloropropane	ug/l	<0,1	-	
*Bromochloromethane	ug/l	<0,1	-	
*1,1,1 Trichlorethane	ug/l	<0,1	-	
*1,1 Dichloropropene	ug/l	<0,1	-	
*Carbon tetrachloride	ug/l	<0,1	-	
*1,2 Dichloroethane	ug/l	<0,1	-	3
*1,2 Dichloropropane	ug/l	<0,1	-	0,15
*Dibromomethane	ug/l	<0,1	-	
*cis 1,3 Dichloropropene	ug/l	<0,1	-	
*trans 1,3 Dichloropropene	ug/l	<0,1	-	
*1,1,2 Trichlorethane	ug/l	<0,1	-	0,2
*1,3 Dichloropropane	ug/l	<0,1	-	
*Chlorobenzene	ug/l	<0,1	-	40
*1,1,1,2 Tetrachloroethane	ug/l	<0,1	-	
*Isopropylbenzene	ug/l	0,3	-	
*bromobenzene	ug/l	<0,1	-	
*n-Propylbenzene	ug/l	<0,1	-	
*2 Chlorotoluene	ug/l	<0,1	-	
*1,3,5 Trimethylbenzene	ug/l	<0,1	-	
*1,2,4 Trimethylbenzene	ug/l	<0,1	-	
*4 Chlorotoluene	ug/l	<0,1	-	
*sec-Butylbenzene	ug/l	<0,1	-	
*1,3 Dichlorobenzene	ug/l	<0,1	-	
*tert-Butylbenzene	ug/l	<0,1	-	

*p-Isopropyltoluene	ug/l	0,4	-		
*1,4 Dichlorobenzene	ug/l	0,2	-	0,5	
*n-butylbenzene	ug/l	<0,1	-		
*1,2 Dichlorobenzene	ug/l	<0,1	-	270	
*1,2 Dibromo-3-chloropropane	ug/l	<0,1	-		
*1,2,4 Trichlorobenzene	ug/l	<0,1	-	190	
*Hexachlorobutadiene	ug/l	<0,1	-	0,15	
*Naphthalene	ug/l	<0,1	-		
*1,2,3 Trichlorobenzene	ug/l	<0,1	-		
*SOMMATORIA Trichlorethene e Tetrachlorethene	ug/l	<0,1	-		EPA 5021A 2014 + EPA 8260D 2018
*Trichlorethene	ug/l	<0,1	-	1,5	
*Tetrachlorethene	ug/l	<0,1	-	1,1	
*NITROBENZENS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Nitrobenzene	ug/l	<0,02	-	3,5	
*1,2-Dinitrobenzene	ug/l	0,05	-	15	
*1,3-Dinitrobenzene	ug/l	0,05	-	3,7	
*1-chloro-2-nitrobenzene	ug/l	<0,02	-		
*1-chloro-3-nitrobenzene	ug/l	<0,02	-		
*1-chloro-4-nitrobenzene	ug/l	<0,02	-		
*Chloronitrobenzens (each one)	ug/l	<0,03	-	0,5	
* SEMIVOLATILE CHLOROBENZENES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Pentachloroethane	ug/l	<0,02	-		
*Hexachloroethane	ug/l	<0,02	-		
*1,2,4-trichlorobenzene	ug/l	<0,02	-	190	
*Hexachloropropene	ug/l	<0,02	-		
*Hexachlorobutadiene	ug/l	<0,02	-		
*Hexachlorociclopentadiene	ug/l	<0,02	-		
*1,2,4,5-tetrachlorobenzene	ug/l	<0,02	-	1,8	
*2-chloronaphtalene	ug/l	<0,02	-		
*Pentachlorobenzene	ug/l	<0,02	-	5	
*Hexachlorobenzene	ug/l	<0,002	-	0,01	
*PHENOLS AND CHLOROPHENOLS		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*2-Chlorophenol	ug/l	<0,02	-	180	
*2,4-Dichlorophenol	ug/l	<0,02	-	110	

*2,4,6-Trichlorophrnol	ug/l	<0,02	-	5	
*Pentachlorophenol	ug/l	<0,02	-	0,5	
*AROMATIC AMINES		-	-		EPA 3510C 1996 + EPA 8270 E 2018
*Aniline	ug/l	<0,02	-	10	
* diphenylamine	ug/l	<0,02	-	910	
*o,p-Toluidine	ug/l	<0,02	-	0,35	
* ORGANOCHLORINATED PESTICIDES		-	-		EPA 3510C 1996 + EPA 8081 B 2007
*pentachlorobenzene	ug/l	<0,0001	-		
*Alpha- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Hexachlorobenzene	ug/l	<0,0001	-		
*Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
*Delta- hexachlorohexane	ug/l	<0,0001	-		
*Eptachlor	ug/l	<0,0001	-		
*Aldrin	ug/l	<0,0001	-	0,03	
*Atrazine	ug/l	<0,0001	-	0,3	
*Alaclor	ug/l	<0,0001	-	0,1	
*Isodrin	ug/l	<0,0001	-		
*Eptaclor Epossid	ug/l	<0,0001	-		
*Endosulfan I	ug/l	<0,0001	-		
*Alpha Chlordane	ug/l	<0,0001	-		
*Gamma Chlordane	ug/l	<0,0001	-		
*Dieldrin	ug/l	<0,0001	-	0,1	
*4-4'-DDE	ug/l	<0,0001	-		
*Endrin	ug/l	<0,0001	-	0,1	
*2,4_DDD	ug/l	<0,0001	-		
*2,4_DDE	ug/l	<0,0001	-		
*2,4-DDT	ug/l	<0,0001	-		
*Endosulfan II	ug/l	<0,0001	-		
*4-4'-DDD	ug/l	<0,0001	-		
*4-4'-DDT	ug/l	<0,0001	-		
* Methoxychlor	ug/l	<0,0001	-		
*Chlordane	ug/l	<0,0001	-	0,1	
*DDD, DDT, DDE	ug/l	<0,0001	-	0,1	
*Sum organochlorinated pesticides	ug/l	<0,001	-	0,5	
**POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-	-		EPA 3510C 1996 + EPA 8082A 2007

*2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		
*2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
*2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
*2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
*2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
*2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
*2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
*2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
*3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
*3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
*2,2',3,5,5',6-HxCB (PCB-151)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-118+149)	ug/l	<0,0004	-		
*2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
*2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
*2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
*2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
*2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
*2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
*3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
*2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
*2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
*2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
*2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
*2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
*2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
*2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
*3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
*2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
*2,3,3',4,4',5,5'-HpCB (PCB-189)	ug/l	<0,0004	-		
* Sum Polichlorobiphenils (PCB)	ug/l	<0,007	-	0,01	
Total Hydrocarbons (expressed as n-hexane	ug/l	<40	95	350	UNI EN ISO 9377-2:2002
* DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001	-		EPA 3546 2007+ EPA 8280B 2007

14.3 Appendix 3 Analytical results of leachates collected in June 2022

DATA SAMPLE

Sample description:	P1
Sampling method:	*D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	50		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	1		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	**#16**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	17		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	25		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<1		5	EPA 7199 1996
*Iron	ug/l	**#2390**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	0,2		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**#22**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	2		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	6		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	1		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**#2630**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	23		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*INORGANIC POLLUTANT		-			
*Boron	ug/l	**#1530**		1000	UNI EN ISO 17294-2:2016
*Nitrites	ug/l	<100		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	1160		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	32		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	

Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenz[a,h]anthracene	ug/l	<0,002	91	0,01	
Benzo[ghi]perylene^	ug/l	<0,01	95	0,01	
Sum PAH (^)	ug/l	<0,01		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,2	90	1	
toluene	ug/l	0,1	88	15	
Ethylbenzene	ug/l	0,1	92	50	
m-xylene p-xylene	ug/l	<0,1	92	10	
Styrene	ug/l	<0,1	86	25	
*TRIHALOMETHANES	ug/l	-			EPA 5021A 2014 + EPA 8260D 2018
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	0,6			
*CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Chloromethane	ug/l	<0,1		1,5	
Trichloromethane	ug/l	<0,5		0,5	
1,2-Dichloroethane	ug/l	<0,1		3	
Trichloroethylene	ug/l	<0,1		1,5	
Tetrachloroethylene	ug/l	<0,1		1,1	
Hexachlorobutadiene	ug/l	<0,1		0,15	
Sum of organohalogens	ug/l	<0,5		10	
*NON CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
1,1-Dichloroethane	ug/l	<0,1		810	
1,2-Dichloroethylene	ug/l	<0,1		60	
1,2-Dichloropropane	ug/l	<0,1		0,15	
1,1,2- Trichloroethane	ug/l	<0,1		0,2	
*CARCINOGENIC HALOGENATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Tribromomethane	ug/l	<0,1		0,3	
*NITROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018

Nitrobenzene	ug/l	<0,002		3,5	
1,2-Dinitrobenzene	ug/l	<0,002		15	
1,3-Dinitrobenzene	ug/l	<0,002		3,7	
Chloronitrobenzenes (each one)	ug/l	<0,003		0,5	
*CHLOROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018
1,2 dichlorobenzene	ug/l	<0,002		270	
1,4 dichlorobenzene	ug/l	<0,002		0,5	
1,2,4-trichlorobenzene	ug/l	<0,002		190	
1,2,4,5 tetrachlorobenzene	ug/l	<0,002		1,8	
pentachlorobenzene	ug/l	<0,002		5	
esachlorobenzene	ug/l	<0,002		0,01	
*PHENOLS AND CHLOROPHENOLS		-			EPA 3510C 1996 + EPA 8270 E 2018
2-Chlorophenol	ug/l	<0,002		180	
2,4-Dichlorophenol	ug/l	<0,002		110	
2,4,6-Trichlorophenol	ug/l	<0,002		5	
Pentachlorophenol	ug/l	<0,002		0,5	
*AROMATIC AMINES		-			EPA 3510C 1996 + EPA 8270 E 2018
Aniline	ug/l	<0,002		10	
p-Toluidine	ug/l	<0,002		0,35	
*PESTICIDES		-			EPA 3510C 1996 + EPA 8081 B 2007
Alfa- hexachlorohexane	ug/l	<0,0001	-	0,1	
Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
Aldrin	ug/l	<0,0001	-	0,03	
Atrazine	ug/l	<0,0001	-	0,3	
Alaclor	ug/l	<0,0001	-	0,1	
Dieldrin	ug/l	<0,0001	-	0,03	
Endrin	ug/l	<0,0001	-	0,1	
Chlordane	ug/l	<0,0001	-	0,1	
DDD, DDT, DDE	ug/l	<0,0003		0,1	
Sum pesticides	ug/l	<0,0005		0,5	
*POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-			EPA 3510C 1996 + EPA 8082A 2007
2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		

2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
2,2',3,5,5',6-HxCB (PCB-151)	ug/l	0,04	-		
2,3',4,4',5-PeCB (PCB-118+149)		<0,0004	-		
2,3',4,4',5-PeCB (PCB-123)	ug/l	0,004	-		
2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
2,3,3',4,4',5,5'-HpCB (PCB-189)		<0,0004	-		
Sum Polichlorobiphenils (PCB)	ug/l	0,004	-	0,01	
*DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001			EPA 3546 2007+ EPA 8280B 2007
Heavy hydrocarbons C >12 (C12-C40)	[n-hexane] ug/l	150	95		UNI EN ISO 9377-2:2002

DATA SAMPLE

Sample description: P4

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	150		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	4		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	1		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	**#15**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	26		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	**#220**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	1,7		5	EPA 7199 1996
*Iron	ug/l	**#4660**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	0,8		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**#74**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	5		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	6		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	2		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**#320**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	42		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*INORGANIC POLLUTANT		-			
*Boron	ug/l	**#2800**		1000	UNI EN ISO 17294-2:2016
*Nitrites	ug/l	<500		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	420		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	<2		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	

Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenz[a,h]anthracene	ug/l	<0,002	91	0,01	
Benzo[ghi]perylene^	ug/l	<0,01	95	0,01	
Sum PAH (^)	ug/l	<0,01		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	**#1,5**	90	1	
toluene	ug/l	3	88	15	
Ethylbenzene	ug/l	3	92	50	
m-xylene p-xylene	ug/l	3	92	10	
Styrene	ug/l	0,2	86	25	
*TRIHALOMETHANES	ug/l	-			EPA 5021A 2014 + EPA 8260D 2018
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	0,5			
*CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Chloromethane	ug/l	<0,1		1,5	
Trichloromethane	ug/l	**#2**		0,5	
1,2-Dichloroethane	ug/l	<0,1		3	
Trichloroethylene	ug/l	<0,1		1,5	
Tetrachloroethylene	ug/l	<0,5		1,1	
Hexachlorobutadiene	ug/l	<0,1		0,15	
Sum of organohalogens	ug/l	3		10	
*NON CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
1,1-Dichloroethane	ug/l	<0,1		810	
1,2-Dichloroethylene	ug/l	0,5		60	
1,2-Dichloropropane	ug/l	**#0,2**		0,15	
1,1,2- Trichloroethane	ug/l	<0,1		0,2	
*CARCINOGENIC HALOGENATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Tribromomethane	ug/l	<0,1		0,3	
*NITROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018

Nitrobenzene	ug/l	<0,002		3,5	
1,2-Dinitrobenzene	ug/l	<0,002		15	
1,3-Dinitrobenzene	ug/l	<0,002		3,7	
Chloronitrobenzenes (each one)	ug/l	<0,003		0,5	
*CHLOROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018
1,2 dichlorobenzene	ug/l	<0,002		270	
1,4 dichlorobenzene	ug/l	<0,002		0,5	
1,2,4-trichlorobenzene	ug/l	<0,002		190	
1,2,4,5 tetrachlorobenzene	ug/l	<0,002		1,8	
pentachlorobenzene	ug/l	<0,002		5	
esachlorobenzene	ug/l	<0,002		0,01	
*PHENOLS AND CHLOROPHENOLS		-			EPA 3510C 1996 + EPA 8270 E 2018
2-Chlorophenol	ug/l	<0,002		180	
2,4-Dichlorophenol	ug/l	<0,002		110	
2,4,6-Trichlorophenol	ug/l	<0,002		5	
Pentachlorophenol	ug/l	<0,002		0,5	
*AROMATIC AMINES		-			EPA 3510C 1996 + EPA 8270 E 2018
Aniline	ug/l	<0,002		10	
p-Toluidine	ug/l	<0,002		0,35	
*PESTICIDES		-			EPA 3510C 1996 + EPA 8081 B 2007
Alfa- hexachlorohexane	ug/l	<0,0001	-	0,1	
Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
Aldrin	ug/l	<0,0001	-	0,03	
Atrazine	ug/l	<0,0001	-	0,3	
Alaclor	ug/l	<0,0001	-	0,1	
Dieldrin	ug/l	<0,0001	-	0,03	
Endrin	ug/l	<0,0001	-	0,1	
Chlordane	ug/l	<0,0001	-	0,1	
DDD, DDT, DDE	ug/l	0,03		0,1	
Sum pesticides	ug/l	0,03		0,5	
*POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-			EPA 3510C 1996 + EPA 8082A 2007
2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		

2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
2,2,3,5-TeCB (PCB-44)	ug/l	0,5	-		
2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
2,2',3,5,5',6-HxCB (PCB-151)	ug/l	0,09	-		
2,3',4,4',5-PeCB (PCB-118+149)		<0,0004	-		
2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	0,004	-		
3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	0,01	-		
2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
2,3,3',4,4',5,5'-HpCB (PCB-189)		<0,0004	-		
Sum Polichlorobiphenils (PCB)	ug/l	**#0,06**	-	0,01	
*DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001			EPA 3546 2007+ EPA 8280B 2007
Heavy hydrocarbons C >12 (C12-C40)	[n-hexane] ug/l	520	95		UNI EN ISO 9377-2:2002

DATA SAMPLE

Sample description:	P5
Sampling method:	*D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	**#270**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	**#6**		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	**#15**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	19		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	**#290**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<1		5	EPA 7199 1996
*Iron	ug/l	**#5350**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	0,5		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**#57**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	5		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	8,7		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	1,5		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**#210**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	57		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*INORGANIC POLLUTANT		-			
*Boron	ug/l	**#2300**		1000	UNI EN ISO 17294-2:2016
*Nitrites	ug/l	<500		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	<400		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	11		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	0,003	88	0,1	

Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenz[a,h]anthracene	ug/l	<0,002	91	0,01	
Benzo[ghi]perylene^	ug/l	<0,01	95	0,01	
Sum PAH (^)	ug/l	<0,01		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	**#1,4**	90	1	
toluene	ug/l	4	88	15	
Ethylbenzene	ug/l	2	92	50	
m-xylene p-xylene	ug/l	2	92	10	
Styrene	ug/l	0,2	86	25	
*TRIHALOMETHANES	ug/l	-			EPA 5021A 2014 + EPA 8260D 2018
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	0,5			
*CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Chloromethane	ug/l	<0,1		1,5	
Trichloromethane	ug/l	<0,5		0,5	
1,2-Dichloroethane	ug/l	<0,1		3	
Trichloroethylene	ug/l	<0,1		1,5	
Tetrachloroethylene	ug/l	<0,1		1,1	
Hexachlorobutadiene	ug/l	<0,1		0,15	
Sum of organohalogens	ug/l	<0,5		10	
*NON CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
1,1-Dichloroethane	ug/l	<0,1		810	
1,2-Dichloroethylene	ug/l	0,2		60	
1,2-Dichloropropane	ug/l	**#0,2**		0,15	
1,1,2- Trichloroethane	ug/l	<0,1		0,2	
*CARCINOGENIC HALOGENATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Tribromomethane	ug/l	<0,1		0,3	
*NITROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018

Nitrobenzene	ug/l	<0,002		3,5	
1,2-Dinitrobenzene	ug/l	<0,002		15	
1,3-Dinitrobenzene	ug/l	<0,002		3,7	
Chloronitrobenzenes (each one)	ug/l	<0,003		0,5	
*CHLOROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018
1,2 dichlorobenzene	ug/l	<0,002		270	
1,4 dichlorobenzene	ug/l	<0,002		0,5	
1,2,4-trichlorobenzene	ug/l	<0,002		190	
1,2,4,5 tetrachlorobenzene	ug/l	<0,002		1,8	
pentachlorobenzene	ug/l	<0,002		5	
esachlorobenzene	ug/l	<0,002		0,01	
*PHENOLS AND CHLOROPHENOLS		-			EPA 3510C 1996 + EPA 8270 E 2018
2-Chlorophenol	ug/l	<0,002		180	
2,4-Dichlorophenol	ug/l	<0,002		110	
2,4,6-Trichlorophenol	ug/l	<0,002		5	
Pentachlorophenol	ug/l	<0,002		0,5	
*AROMATIC AMINES		-			EPA 3510C 1996 + EPA 8270 E 2018
Aniline	ug/l	<0,002		10	
p-Toluidine	ug/l	<0,002		0,35	
*PESTICIDES		-			EPA 3510C 1996 + EPA 8081 B 2007
Alfa- hexachlorohexane	ug/l	<0,0001	-	0,1	
Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
Aldrin	ug/l	<0,0001	-	0,03	
Atrazine	ug/l	<0,0001	-	0,3	
Alaclor	ug/l	<0,0001	-	0,1	
Dieldrin	ug/l	<0,0001	-	0,03	
Endrin	ug/l	<0,0001	-	0,1	
Chlordane	ug/l	<0,0001	-	0,1	
DDD, DDT, DDE	ug/l	0,008		0,1	
Sum pesticides	ug/l	0,008		0,5	
*POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-			EPA 3510C 1996 + EPA 8082A 2007
2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		

2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
2,2,3,5-TeCB (PCB-44)	ug/l	1,8	-		
2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
2,2',3,5,5',6-HxCB (PCB-151)	ug/l	0,11	-		
2,3',4,4',5-PeCB (PCB-118+149)		<0,0004	-		
2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	0,003	-		
2,3,3',4,4',5,5'-HpCB (PCB-189)		<0,0004	-		
Sum Polichlorobiphenils (PCB)	ug/l	**#1,9**	-	0,01	
*DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001			EPA 3546 2007+ EPA 8280B 2007
Heavy hydrocarbons C >12 (C12-C40)	[n-hexane] ug/l	410	95		UNI EN ISO 9377-2:2002

DATA SAMPLE

Sample description: P6

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	22		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	**#15**		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	**#29**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	17		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	36		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<1		5	EPA 7199 1996
*Iron	ug/l	**#3960**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	0,2		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**#24**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	3,2		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	6		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	0,9		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**#1580**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	60		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*INORGANIC POLLUTANT		-			
*Boron	ug/l	**#1700**		1000	UNI EN ISO 17294-2:2016
*Nitrites	ug/l	<100		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	1000		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	15		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	

Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenz[a,h]anthracene	ug/l	<0,002	91	0,01	
Benzo[ghi]perylene^	ug/l	<0,01	95	0,01	
Sum PAH (^)	ug/l	<0,01		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,7	90	1	
toluene	ug/l	<0,1	88	15	
Ethylbenzene	ug/l	0,1	92	50	
m-xylene p-xylene	ug/l	0,1	92	10	
Styrene	ug/l	<0,1	86	25	
*TRIHALOMETHANES	ug/l	-			EPA 5021A 2014 + EPA 8260D 2018
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	0,6			
*CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Chloromethane	ug/l	<0,1		1,5	
Trichloromethane	ug/l	<0,5		0,5	
1,2-Dichloroethane	ug/l	<0,1		3	
Trichloroethylene	ug/l	<0,1		1,5	
Tetrachloroethylene	ug/l	<0,1		1,1	
Hexachlorobutadiene	ug/l	<0,1		0,15	
Sum of organohalogens	ug/l	<0,5		10	
*NON CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
1,1-Dichloroethane	ug/l	<0,1		810	
1,2-Dichloroethylene	ug/l	<0,1		60	
1,2-Dichloropropane	ug/l	<0,1		0,15	
1,1,2- Trichloroethane	ug/l	<0,1		0,2	
*CARCINOGENIC HALOGENATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Tribromomethane	ug/l	<0,1		0,3	
*NITROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018

Nitrobenzene	ug/l	<0,002		3,5	
1,2-Dinitrobenzene	ug/l	<0,002		15	
1,3-Dinitrobenzene	ug/l	<0,002		3,7	
Chloronitrobenzenes (each one)	ug/l	<0,003		0,5	
*CHLOROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018
1,2 dichlorobenzene	ug/l	<0,002		270	
1,4 dichlorobenzene	ug/l	<0,002		0,5	
1,2,4-trichlorobenzene	ug/l	<0,002		190	
1,2,4,5 tetrachlorobenzene	ug/l	<0,002		1,8	
pentachlorobenzene	ug/l	<0,002		5	
esachlorobenzene	ug/l	<0,002		0,01	
*PHENOLS AND CHLOROPHENOLS		-			EPA 3510C 1996 + EPA 8270 E 2018
2-Chlorophenol	ug/l	<0,002		180	
2,4-Dichlorophenol	ug/l	<0,002		110	
2,4,6-Trichlorophenol	ug/l	<0,002		5	
Pentachlorophenol	ug/l	<0,002		0,5	
*AROMATIC AMINES		-			EPA 3510C 1996 + EPA 8270 E 2018
Aniline	ug/l	<0,002		10	
p-Toluidine	ug/l	<0,002		0,35	
*PESTICIDES		-			EPA 3510C 1996 + EPA 8081 B 2007
Alfa- hexachlorohexane	ug/l	<0,0001	-	0,1	
Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
Aldrin	ug/l	<0,0001	-	0,03	
Atrazine	ug/l	<0,0001	-	0,3	
Alaclor	ug/l	<0,0001	-	0,1	
Dieldrin	ug/l	<0,0001	-	0,03	
Endrin	ug/l	<0,0001	-	0,1	
Chlordane	ug/l	<0,0001	-	0,1	
DDD, DDT, DDE	ug/l	<0,0003		0,1	
Sum pesticides	ug/l	<0,0005		0,5	
*POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-			EPA 3510C 1996 + EPA 8082A 2007
2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		

2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
2,2',3,5,5',6-HxCB (PCB-151)	ug/l	<0,0004	-		
2,3',4,4',5-PeCB (PCB-118+149)		<0,0004	-		
2,3',4,4',5-PeCB (PCB-123)	ug/l	<0,0004	-		
2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
2,3,3',4,4',5,5'-HpCB (PCB-189)		<0,0004	-		
Sum Polichlorobiphenils (PCB)	ug/l	<0,007	-	0,01	
*DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001			EPA 3546 2007+ EPA 8280B 2007
Heavy hydrocarbons C >12 (C12-C40)	[n-hexane] ug/l	300	95		UNI EN ISO 9377-2:2002

DATA SAMPLE

Sample description: P2

Sampling method: *D.Lgs 152/2006 + APAT CNR IRSA 1030 Man 29 2003 + PGQ14 Rev.05

ANALITYCAL RESULTS

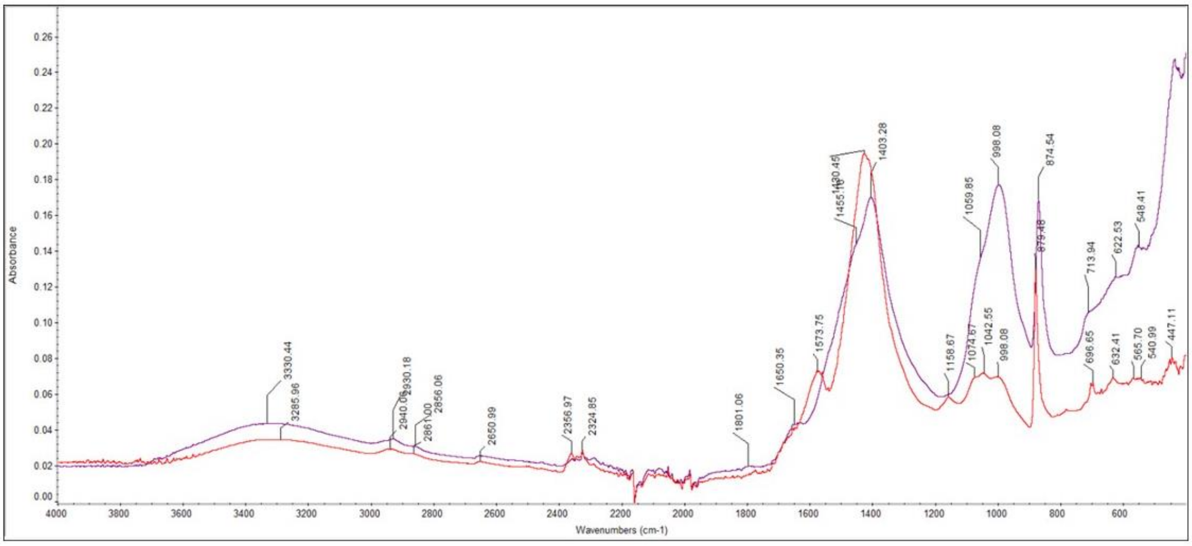
ANALYTICAL TEST	UNITY OF MEASUREMENTS	VALUES	RECOVERY % (R)	LIMIT VALUES	METHODIC
*METALS					
*Aluminum	ug/l	104		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Antimony	ug/l	1,3		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Silver	ug/l	<0,6		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Arsenic	ug/l	**#20**		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Beryllium	ug/l	<0,6		4	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cadmium	ug/l	<0,6		5	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Cobalt	ug/l	17		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Total chromium	ug/l	30		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Hexavalent chromium	ug/l	<1		5	EPA 7199 1996
*Iron	ug/l	**#3970**		200	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Mercury	ug/l	0,2		1	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Nickel	ug/l	**#24**		20	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Lead	ug/l	4,2		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Copper	ug/l	11		1000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Selenium	ug/l	1,1		10	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Manganese	ug/l	**#2140**		50	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Thallium	ug/l	<0,6		2	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*Zinc	ug/l	29		3000	UNI EN ISO 15587-2:2002 + UNI EN ISO 17294-2:2016
*INORGANIC POLLUTANT		-			
*Boron	ug/l	**#1680**		1000	UNI EN ISO 17294-2:2016
*Nitrites	ug/l	<100		500	APAT CNR IRSA 4050 Man 29 2003
*Fluorides	ug/l	1140		1500	APAT CNR IRSA 4050 Man 29 2003
*Sulfates	mg/l	27		250	APAT CNR IRSA 4050 Man 29 2003
POLYCYCLIC AROMATIC HYDROCARBONS		-			EPA 3510C 1996 + EPA 8270 E 2018
Pyrene	ug/l	<0,002	97	50	
Benz[a]anthracene	ug/l	<0,002	96	0,1	
Chrysene	ug/l	<0,002	91	5	
Benzo[b]fluoranthene^	ug/l	<0,002	88	0,1	

Benzo[k]fluoranthene^	ug/l	<0,002	98	0,05	
Benzo[a]pyrene	ug/l	<0,002	92	0,01	
Indeno[1,2,3-cd]pyrene^	ug/l	<0,002	98	0,1	
Dibenz[a,h]anthracene	ug/l	<0,002	91	0,01	
Benzo[ghi]perylene^	ug/l	<0,01	95	0,01	
Sum PAH (^)	ug/l	<0,01		0,1	
AROMATIC ORGANIC COMPOUNDS		-			EPA 5021A 2014 + EPA 8260D 2018
benzene	ug/l	0,3	90	1	
toluene	ug/l	0,1	88	15	
Ethylbenzene	ug/l	0,1	92	50	
m-xylene p-xylene	ug/l	0,1	92	10	
Styrene	ug/l	<0,1	86	25	
*TRIHALOMETHANES	ug/l	-			EPA 5021A 2014 + EPA 8260D 2018
*Bromodichloromethane	ug/l	<0,1		0,17	
*Dibromochloromethane	ug/l	<0,1		0,13	
*Bromoform	ug/l	<0,1		0,3	
*Sum trihalomethanes	ug/l	0.6			
*CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Chloromethane	ug/l	<0,1		1,5	
Trichloromethane	ug/l	<0,5		0,5	
1,2-Dichloroethane	ug/l	<0,1		3	
Trichloroethylene	ug/l	<0,1		1,5	
Tetrachloroethylene	ug/l	<0,1		1,1	
Hexachlorobutadiene	ug/l	<0,1		0,15	
Sum of organohalogens	ug/l	<0,4		10	
*NON CARCINOCENIC CHLORINATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
1,1-Dichloroethane	ug/l	<0,1		810	
1,2-Dichloroethylene	ug/l	<0,1		60	
1,2-Dichloropropane	ug/l	<0,1		0,15	
1,1,2- Trichloroethane	ug/l	<0,1		0,2	
*CARCINOGENIC HALOGENATED ALIPHATICS		-			EPA 5021A 2014 + EPA 8260D 2018
Tribromomethane	ug/l	<0,1		0,3	
*NITROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018

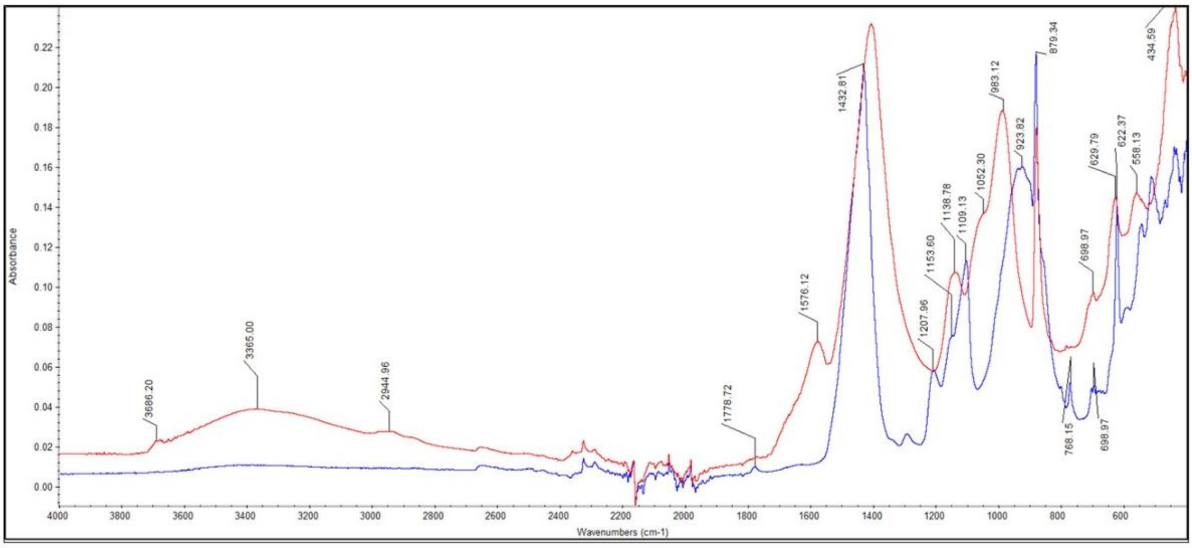
Nitrobenzene	ug/l	<0,002		3,5	
1,2-Dinitrobenzene	ug/l	<0,002		15	
1,3-Dinitrobenzene	ug/l	<0,002		3,7	
Chloronitrobenzenes (each one)	ug/l	<0,003		0,5	
*CHLOROBENZENES		-			EPA 3510C 1996 + EPA 8270 E 2018
1,2 dichlorobenzene	ug/l	<0,002		270	
1,4 dichlorobenzene	ug/l	<0,002		0,5	
1,2,4-trichlorobenzene	ug/l	<0,002		190	
1,2,4,5 tetrachlorobenzene	ug/l	<0,002		1,8	
pentachlorobenzene	ug/l	<0,002		5	
esachlorobenzene	ug/l	<0,002		0,01	
*PHENOLS AND CHLOROPHENOLS		-			EPA 3510C 1996 + EPA 8270 E 2018
2-Chlorophenol	ug/l	<0,002		180	
2,4-Dichlorophenol	ug/l	<0,002		110	
2,4,6-Trichlorophenol	ug/l	<0,002		5	
Pentachlorophenol	ug/l	<0,002		0,5	
*AROMATIC AMINES		-			EPA 3510C 1996 + EPA 8270 E 2018
Aniline	ug/l	<0,002		10	
p-Toluidine	ug/l	<0,002		0,35	
*PESTICIDES		-			EPA 3510C 1996 + EPA 8081 B 2007
Alfa- hexachlorohexane	ug/l	<0,0001	-	0,1	
Beta- hexachlorohexane	ug/l	<0,0001	-	0,1	
Gamma- hexachlorohexane	ug/l	<0,0001	-	0,1	
Aldrin	ug/l	<0,0001	-	0,03	
Atrazine	ug/l	<0,0001	-	0,3	
Alaclor	ug/l	<0,0001	-	0,1	
Dieldrin	ug/l	<0,0001	-	0,03	
Endrin	ug/l	<0,0001	-	0,1	
Chlordane	ug/l	<0,0001	-	0,1	
DDD, DDT, DDE	ug/l	<0,0003		0,1	
Sum pesticides	ug/l	<0,0005		0,5	
*POLICHLOROBIPHENILS (PCB dioxin like + other PCB)		-			EPA 3510C 1996 + EPA 8082A 2007
2,2,5-TrCB (PCB-18)	ug/l	<0,0004	-		

2,4,4'-TrCB (PCB-28)	ug/l	<0,0004	-		
2,4,5-TrCB (PCB-31)	ug/l	<0,0004	-		
2,2',5,5'-TeCB (PCB-52)	ug/l	<0,0004	-		
2,2,3,5-TeCB (PCB-44)	ug/l	<0,0004	-		
2,2',3,5',6-PeCB (PCB-95)	ug/l	<0,0004	-		
2,2',4,5,5'-PeCB (PCB-101)	ug/l	<0,0004	-		
2,2',4,4',5-PeCB (PCB-99)	ug/l	<0,0004	-		
3,4,4',5-TeCB (PCB-81)	ug/l	<0,0004	-		
3',3,4,4'-TeCB (PCB-77+110)	ug/l	<0,0004	-		
2,2',3,5,5',6-HxCB (PCB-151)	ug/l	0,05	-		
2,3',4,4',5-PeCB (PCB-118+149)		<0,0004	-		
2,3',4,4',5-PeCB (PCB-123)	ug/l	0,004	-		
2,3,4,4',5-PeCB (PCB-114)	ug/l	<0,0004	-		
2,2',3,4',5,5'-HxCB (PCB-146)	ug/l	<0,0004	-		
2,2',4,4',5,5'-HxCB (PCB-153)	ug/l	<0,0004	-		
2,3,3',4,4'-PeCB (PCB-105)	ug/l	<0,0004	-		
2,2',3,4,4',5'-HxCB (PCB-138)	ug/l	<0,0004	-		
3,3',4,4',5-PeCB (PCB-126)	ug/l	<0,0004	-		
2,2',3,4',5,5',6-HpCB (PCB-187)	ug/l	<0,0004	-		
2,2',3,4,4',5',6-HpCB (PCB-183)	ug/l	<0,0004	-		
2,3',4,4',5,5'-HxCB (PCB-167+128)	ug/l	<0,0004	-		
2,2',3,3',4',5,6-HpCB (PCB-177)	ug/l	<0,0004	-		
2,3,3',4,4',5-HxCB (PCB-156)	ug/l	<0,0004	-		
2,3,3',4,4',5'-HxCB (PCB-157)	ug/l	<0,0004	-		
2,2',3,4,4',5,5'-HpCB (PCB-180)	ug/l	<0,0004	-		
3,3',4,4',5,5'-HxCB (PCB-169)	ug/l	<0,0004	-		
2,2',3,3',4,4',5-HpCB (PCB-170)	ug/l	<0,0004	-		
2,3,3',4,4',5,5'-HpCB (PCB-189)		<0,0004	-		
Sum Polichlorobiphenils (PCB)	ug/l	0,005	-	0,01	
*DIOXINE AND FURANS – Sum PCDD-PCDF	ug/l	<0,00001			EPA 3546 2007+ EPA 8280B 2007
Heavy hydrocarbons C >12 (C12-C40)	[n-hexane] ug/l	230	95		UNI EN ISO 9377-2:2002

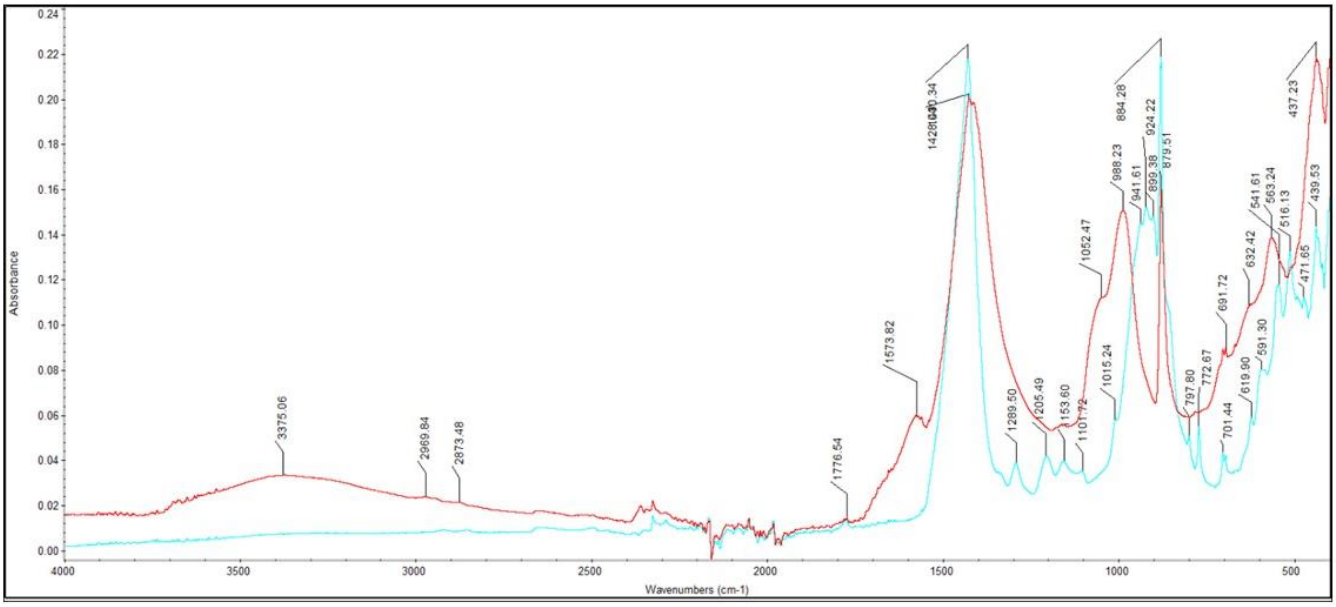
14.4 Appendix 4: ATR-IR spectra on dried and calcined leachate samples



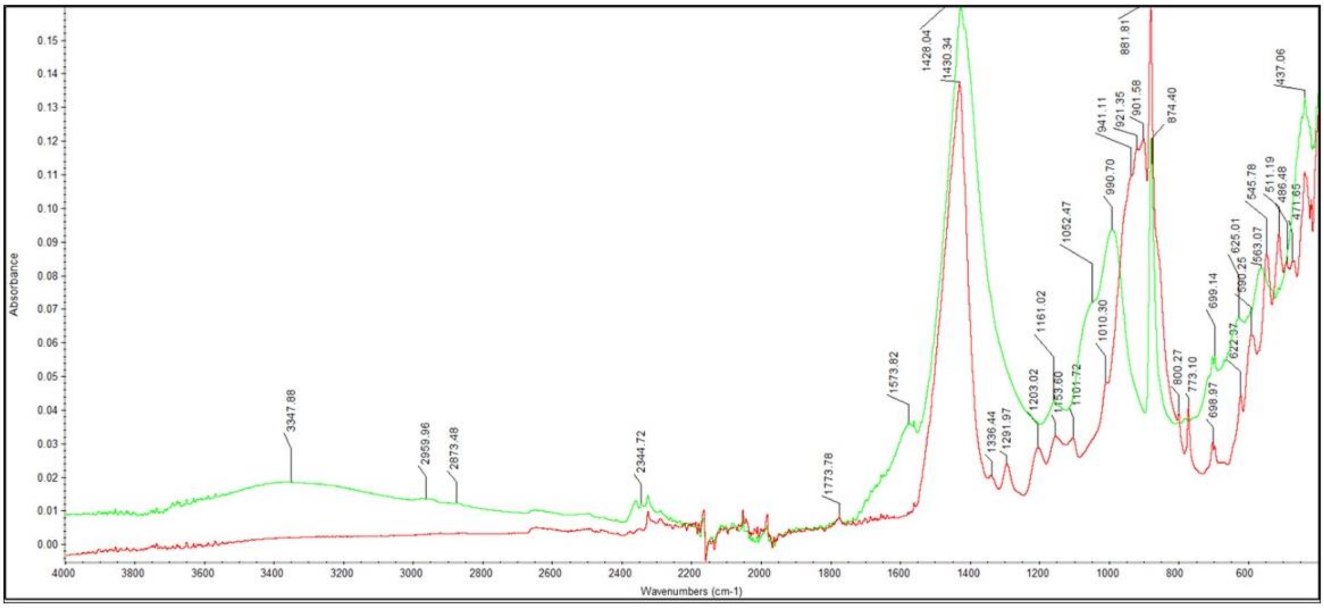
ATR-IR spectra of dried P5 (red) and washed (violet).



ATR-IR spectra of dried (red) and calcinated (blue) P1.



ATR-IR spectra of dried (red) and calcinated (light blue) P6.



ATR-IR spectra of dried (green) and calcinated (red) P2.