PROSODOL

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STRATEGIES TO IMPROVE AND PROTECT SOIL QUALITY FROM THE DISPOSAL OF OLIVE OIL MILLS WASTES IN THE MEDITERRANEAN

Life

Good Practices for the Agronomic Use of Olive Mill Wastes

Application Guide

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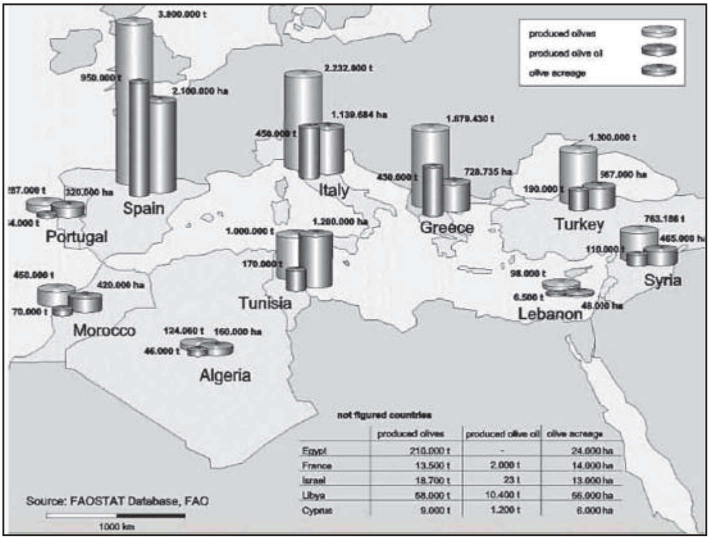
OLIVE OIL PRODUCTION IN THE MEDITERRANEAN REGION

The olive tree plays a vital role in the economy, ecology and social life of the Mediterranean countries, where approximately 8.5 million ha are in production, corresponding to 98% of the world olive cultivation. Spain, Italy and Greece account for around 75% of olive oil world production, which is almost 2.8 million tons, while the rest originates mainly from Portugal, Tunisia, Marocco, Algeria, Turkey, the Middle East region, and Australia.



Exports	Imports
1. Spain	Italy
2. Italy	USA
3. Tunisia	France
4. Greece	Germany
5. Portugal	UK
6. Turkey	Brazil
7. Argentina	Portugal
8. France	Japan
9. Australia	Canada
10. Egypt	Spain

OLIVE MILL WASTES

The by-products derived from the oil production process are different for the different technologies used for oil extraction.

In specific and except oil:

Traditional press system → produces wastewater and olive press-cake

3-phases centrifugation system → produces wastewater and olive cake

2-phases centrifugation system → produces a mixture of wastewater and olive cake

The composition of Olive Mill Wastes is not constant - both qualitatively and quantitatively-and it varies according to:

- ✓ soil and climate conditions of the pro duction site
- ✓ olive cultivar
- ✓ ripening state of the olives
- ✓ composition of the vegetation water
- ✓ olive oil extraction process
- ✓ storage time

Olive Mill Wastewater (OMWW)

OMWW is a mixture of:

- ✓ vegetation water
- ✓ water used in the various stages of the oil extraction process, i.e. water added during cen-trifugation, water from filtering disks, and from washing rooms and equipment
- ✓ soft tissues of the olive fruit

The OMWW is characterized by:

- ✓ intensive violet-dark brown up to black color
- ✓ strong offensive smell
- ✓ pH between 3 and 6 (slightly acid)
- ✓ high electrical conductivity
- ✓ high degree of organic pollution
- ✓ high content of polyphenols
- ✓ high content of solid matter

Olive Mill Wastes comprise serious threat for the environment and should not be disposed untreated on soil, in sea, in rivers, in streams or in wells.

Characteristic parameters of Olive Mill Wastewater are included in Table 1 of Annex 1

Typically, OMWW contains 80-96% water, 3.5-15% organics and 0.5-2% mineral salts.

The organic fraction includes sugars, polyphenols, polyalcohols, pectins and lipids, nitrogenous compounds, organic acids, carotenoids and almost all water soluble constituents of olives.

The inorganic fraction contains chloride, sulphate and phosphoric salts of potassium and calcium, iron, magnesium, sodium, copper and other trace elements in various chemical forms.

Olive Husk

The chemical composition of olive husk (also known as olive pomace or olive cake) varies within very large limits according to type, condition, and origin of olives, as well as to olive oil extraction process.

Olive husk contains crushed stones, skin, pulp, water and a remaining quantity of oil. Olive husk is also characterized by its phytotoxicity, hydro-phobicity, salinity, low pH and polyphenols. The presence of phenols as well as short and long chain fatty acids is considered to be responsible for the phytotoxicity and antimicrobial nature of olive husk.

The exhausted olive cake (de-oiled olive cake) is a dry material (8–10% moisture) composed of ground olive stones and pulp. The exhausted olive cake has a high lignin, cellulose, and hemicellulose content.

Chemical composition of olive husks derived from press and from 3-phase extraction systems are included in Table 2 of Annex 1

Two Phases Olive Mill Wastes (TPOMW)

The continuous centrifuge two-phase process generates a liquid phase (olive oil) and organic slurry (two-phase olive mill waste-TPOMW). This semi-solid waste (also known as olive wet cake, olive wet husk or olive wet pomace) has a strong odour and doughy texture. Similarly to olive cake, TPOMW is composed by the skin, pulp and crahed stones of the olive but it also contains vegetation water increasing the moisture content up to 50-70%. This residue is characterised by slightly acidic pH, high organic matter concentration (mainly of lignocellu-loseic origin) and the presence of valuable nutrients, especially K.

TPOMW is a phytotoxic material due to the presence of high concentrations of polyphenols, lipids and organic acids, making its disposal a major environmental problem in Mediterra-nean countries, where the accumulation of these hazardous wastes is an important source of soil and water pollution and toxicity. On the other hand, TPOMW has very high organic mat-ter content (up to 92%), therefore its controlled recycling as amendment to agricultural soils and mainly to soils poor in organic matter, as Mediterranean soils are, has been proposed as a solution for TPOMW management.

Inorganic constituents may potentially serve as sources of plant nutrients, improve soil fertility and render Olive Oil Mill Wastes suitable for re-use as soil amendment, however,

only under specific preconditions and limitations

DISPOSAL OF OLIVE MILL WASTEWATER

OMWW output corresponds roughly to 50-60 % of the weight of olives processed through discontinuous extraction plants (extraction obtained by pressure) and to the overall weight of olive processed through continuous 3-phase extraction plants because of the water added during the processes.

Two-phase extraction systems allow a significant reduction in OMWW production but on the other hand very wet olive husks are produced which are hardly suitable for husk oil extrac-tion.

OMWW properties may vary during storage because of the sedimentation process of the in-soluble fraction, the transformation of the organic matter carried out by microorganisms and the evaporation of the water fraction. Specifically, the concentration of easily fermentable organic compounds is decreased thanks to the action of decomposing microorganisms, pH normally increases, BOD5 and the quantity of suspended solids decrease.

In general, OMWW have:

- High Biological Oxygen Demand (BOD)
- High Chemical Oxygen Demand (COD)
- High content of Organic Matter
- High content of suspended solids
- High content of lipids and phenols
- Medium to high content of mineral susbstances, mainly potassium, phosphorous, calcium

From a microbiological point of view OMWW contain mainly bacteria (mostly cellulolitic and not nitrificant) but also yeasts and fungi.

Despite the absence of toxic compounds or pathogens, OMWW can cause serious problems, especially to waters, because of their low pH values and their high content in salts and organic matter.

This is the reason why:

OMWW must not be disposed directly into the sewage system without the application of specific treatments aimed to lower the polluting potential

Specific disposal areas (i.e. evaporation ponds or lagoons) is a practice spread in Greece, however not in Italy and Spain because of environmental constraints and the extremely slow evaporation rate.

Disposal in evaporation lagoons

Direct disposal on soil

LEGISLATION

The Italian law

The Italian Law **N° 574 of 1996** together with the **Ministry Decree 6 July 2005** defines the terms for the reutilization in field of the OMWW and of the olive husks.
In specific:

The law sets the limit that can be applied each year on a soil according to the thresholds:
→ 50m^3/ha for OMWW obtained from discontinuous extraction systems (press systems)
→ 80m^3/ha for OMWW obtained from continuous extraction systems (3-phase systems)

The application of the OMWW on soil in specific area should be previously announced to the Mayor of the city and at least 30 days in advance

The law specifies the soil categories on which the OMWW must NOT be applied:
→ Soils which are less than 300meters away from preservation areas for water collection destined to human consumption
→ Soils which are less 200 meters away from inhabited areas
→ Soils which are cultivated with vegetable crops
→ Soils where watertable is less than 10 meters deep
→ Soils which are frozen, covered by snow, awashed or saturated with water

The OMWW can be stocked for **NO MORE** than 30 days before utilization

Olive husks can be used as amendments with no specific limitations **IF** they comply with the Italian law No 748 of 1984, D.M. 27 March 1998 and D.M. 3 November 2004 and following modifications and updates, regulating the use of soil amendments

The law defines also the authorities which are responsible for the supervision and controlling of OMWW application

The Legislative Decree **N° 152 of 1999**, transposition of the European Directives 91/271/CEE and 91/676/CEE, regulates the waters safeguard from pollution. The article 38 of this act makes reference to the Italian Law n°574 of 1996 with regards to agronomic use of sewage sludge and other wastes such as olive mill wastes. The same law regulates the disposal of wastes directly in the sewage system setting the thresholds of the chemical and physical parameters the wastes must comply with.

Spanish legislation

In Spain only the Regional Government of Andalusia has enacted a law about the use of OMWW as fertilizer in agriculture (Decree 4/2011). This regional law is based in the Italian one. In particular, Art. 7 specifies that:

- ✓ The volume of effluent to be applied to agricultural land exceeds in no case the amount of 50 m3/ha/year.
- ✓ Applications should be designed so as not to produce surface runoff, leaching, or invasive lesions of the soil water table.
- ✓ The field application of effluent shall be subject to the following areas of exclusion:
- ◆ *located within 500 meters copared to urban areas.*
- ◆ *the police zone 100 meters above the public water mastery, defined in Article 6.2.b of Regulation for Public Water, approved by Royal Decree 849/1986 of 11 April.*
- ◆ *the easement area of protection of 100 meters above the Shoreline Public Domain, as defined in Article 23.1 of Law 22/1988 of 28 July, Costas.*

A Portuguese law was established in 2000 (Law No. 626/2000) which the olive oil mills wastewater is permitted to be disposed on soil at a maximum amount of 80m^3/ha annually.

Greek legislation

In Greece there are no specific regulations regarding the discharge of olive mill wastewater. The main principles for olive mill wastewater management are based on the **Law 1650/86** *"For the Protection of the Environment"* according to which, olive mill owners are obliged to provide an environmental impact assessment study.

The updated circular letter YM/5784/23-1-1992 (No 4419/23-10-1992) refers to the problems encountered due to olive mill wastewater disposal, the need for an efficient pre-treatment and the care required in order to avoid disposal to various water resources. The present legislative status in Greece (Laws 1650/86 and 3010/2002) does not allow application of untreated olive mill wastes to soil surface.

Each Greek Region is responsible for adopting proper OMWW management practices, encouraging different waste management approaches

Cyprus legislation

Of particular interest is the case of Cyprus as there is special legislative act for oil olive waste, and in particular the **Cyprus Ordinance No. 254/2003** of 1 November 2004 on Water Pollution Control (Waste Disposal Permit)

Ordinance of 2003. The waste streams generated by olive mills differ according to the process used for the oil extraction; i.e. if is two-phase or three-phase centrifuge and the types and amounts of waste allowed to be deposited are specifically defined.

Regardless the type of process they originate from (two-phase or three-phase):

- ◆ Liquid wastes should be temporarily stored in waterproof sealed tanks. Whether or not the streams are mixed or separated depends on the method of disposal.
- ◆ Sludge should be temporarily stored in a covered area with concrete base (platform). Liquids originating from leakages or run-offs from the temporary storage areas for the solid wastes or sludge should be collected and transferred to the liquid wastes tanks, via open-air waterproof pipes.

Waste stream, liquid waste from the washing of the olives: can be used for irrigation of cultivations (trees, forest-trees, etc) surrounding the olive mill. In cases that the waste is mixed with liquid waste originating from the centrifuging decanters, the liquid wastes should be transferred for final disposal in evaporation tanks. Evaporation tanks should be open, waterproof, earthen and shallow; i.e. maximum depth of 1.2 m. Liquid wastes should be transferred to the evaporation tank within closed pipes or with a tanker. The required quality of the liquid wastes to be disposed in the evaporation tank is shown in the table below (maximum allowance).

Quality of liquid waste entering the evaporation tank in Cyprus

Parameter	Maximum value allowed
pH	5.0 – 7.0
Electric conductivity	10,000 μS/cm
Suspended solids	5,000 mg/l
BOD5	10,000 mg/l
Fat	6,000 mg/l
Phenols	1,000 mg/l

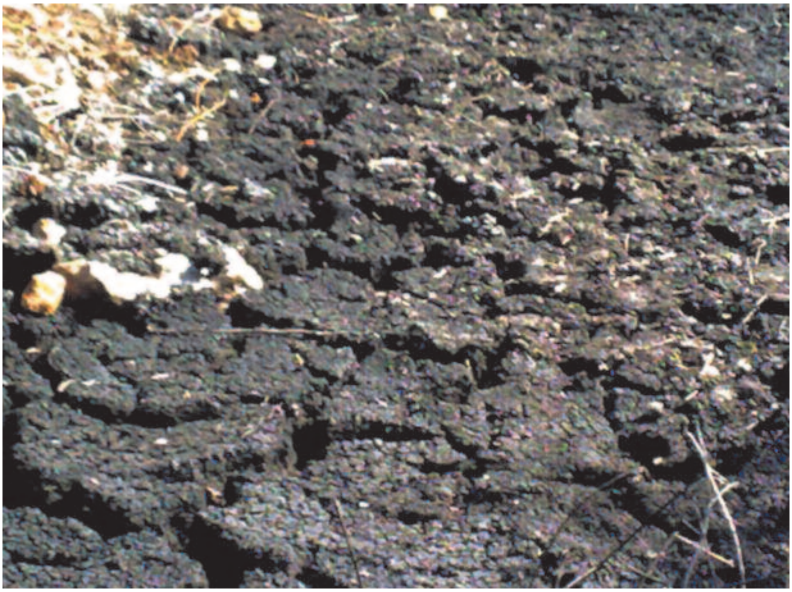
Sludge produced by the decanter of a two-phase mill, should be collected and transferred by a tanker to the appropriate facilities for incineration or composting. At the end of functioning period, no sludge should be present at the temporary storage area.

The institution exploiting the waste, should maintain a database for the quantities and the ways the waste has been disposed.

Solid wastes produced by a three-phase mill should be collected and used as animal stocking or fertiliser or sent to a seed-oil production facility for further treatment.

If olive dregs are going to be used as soil improver (fertiliser), the application should be at least 300m from residential areas, with maximum disposal rate 3.5 tonnes/ ha/ year.

At the end of functioning period **NO SLUDGE** or **SOLID WASTE** should be present at the temporary storage area



Sludge depositing at the bottom of the evaporation tanks, should be collected when needed after the liquid present in the tank has been dried, and transferred for disposal to an approved public area or be used as soil improver

USE OF WASTEWATER FOR IRRIGATION

Olive mill wastewaters could be used for olive oil trees irrigation and the general improvement of soil fertility thanks to their content in organic matter and nutrients. However, **keep always in mind** that OMWWs are wastes with very high concentration in polyphenols and other organic substances as well as inorganics that may cause serious soil degradation, **IF** specific precausions are not **STRICTLY** followed.

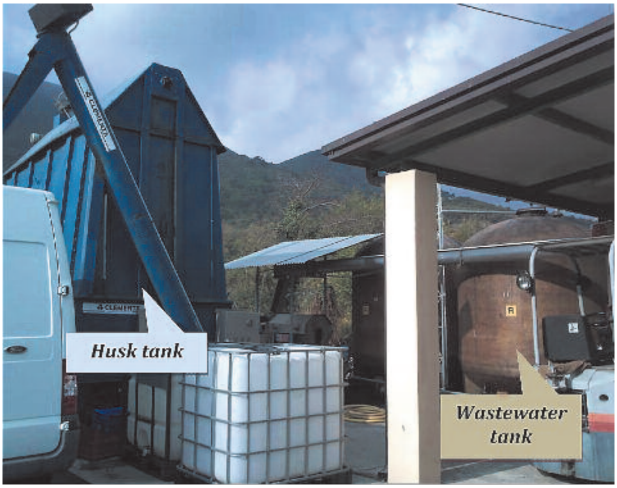
The implementation of the instructions of this chapter involves the use of only wastewater and, therefore, it is preassumed that after oil production **the wastes have been separated into wastewater and husk.**

By-products deriving from olive processing are normally rich in Potassium and, to a lesser extent, in other nutrients (Nitrogen, Phosphorous, Calcium, Magnesium).

Therefore, they can replace / integrate the nutritional elements provided through fertilization. Besides, the high content in organic matter allows for an improvement of the soil chemical / physical properties.

However, spreading of OMWW on soil could pose some disadvantages to soil properties because of the characteristics of the wastes.

The Italian olive oil producers (using a 3-phase extraction system) separate the produced wastes into wastewater and husks. They use two different tanks at the end of the production system, one for wastewater and one for husks.



Notwithstanding, soil is a very reactive matrix that can mitigate some of such disadvantages:

- it holds the suspended compounds as a filter: clay, humus and organic colloids can bind mineral salts;
- it contains microorganisms that allow quick degradation of organic compounds e.g. polyphenols and lipids;
- can increase polyphenols degradability thus lowering their phytotoxic effect thanks to the air it holds inside and the light that hits soil surface.

ITALY is the first European country that has established, since 1996, specific law for the disposal of mill wastes on soil

From relevant research activities it comes out that the spread of moderate quantities of olive mill wastes on soils - carried out in the ways and at the quantities set by the **ITALIAN law** - does not cause damages to crops nor does it modify key soil properties or the microflora composition for more than few months.

Olive Mill Wastes can be considered as soil amendments

Benefits derived from the agronomic use of Olive Mill Waste

Money saving: soil spreading is still the cheapest way for the disposal of Olive Mill Wastes

The possibility to fully automate, under certain conditions, the distribution of OMWW (e.g. when certain crops such as cereals are present near the olive mill)

Reduction of the impacts deriving from high energy demanding plants for Olive Mill Wastes purification and from the subsequent disposal of the sludge or of other residues obtained from these processes

The partial recycling of essential nutrients which can be retained by crops through the input of organic matter, exchangeable potassium and, at a lesser extent, phosphorous and magnesium, so that smaller quantities of chemical fertilizers need to be applied

Olive tree irrigation

In order to take full advantage of the benefits avoiding potential negative impacts on crops and environment, few and simple rules should be adopted for the safe distribution of OMWW on soil:

- OMWWs should be spread as they come immediately after their production; if this is not possible due to logistics reasons, it is necessary to stock them in appropriate containers for no more than 1 month

- observe thresholds set by the law (if available) or those set in the literature world-wide (Annex 2): besides not being charged of a fee, the relevant amounts distributed will not have any phytotoxic effect on plants, neither will they be harmful (according to the literature available)

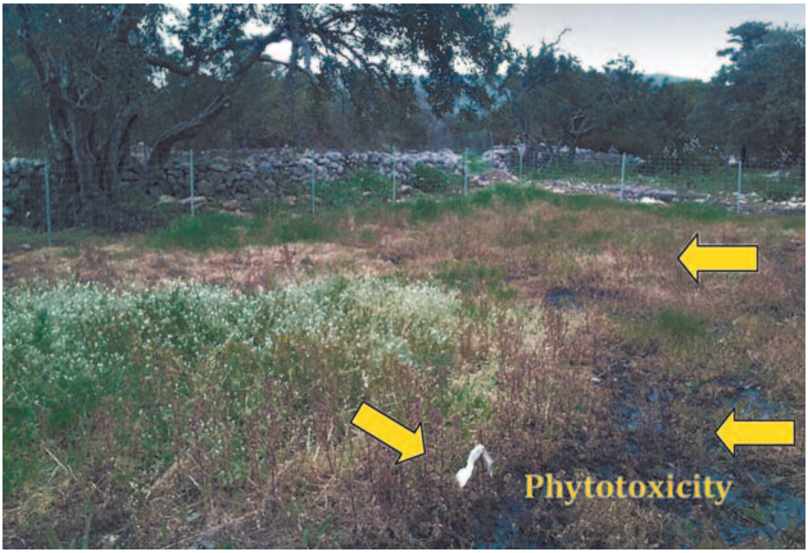
- distribution on soil surface should be uniform

- if needed, provide soil tillage after wastes spread in order to avoid bad odours and to incorporate the waste into the soil

- careful evaluation of soil properties:

◆ it is better to spread wastes on a soil with high pH and rich in carbonates in or-der to avoid excessive acidification of soil. Anyway, acidification occurs immediately after the spread of OMWW but it tends to vanish in few months[1]

[1] This is mainly due to two factors: (a) OMWWs contain very high concentration of potassium, which especially in clay soil, enters the cation exchange system originating reactions of alkaline hydrolysis; (b) significant production of ammonia due to bacterial degradation of organic compounds contained in the OMWWs themselves.



Phytotoxicity due to OMWW disposal on soil

◆ it is better to avoid soils rich in salts because of the possible reduction of the stability of soil aggregate and the consequent deterioration of soil structure

◆ reduce the amount of OMWW distributed if the hydraulic conductivity is < 5 mm/hour in order to avoid runoff of waters;

➔ carefully choose when to distribute OMWs, taking into account rainfall and special features of crops. Best results can be achieved when:

◆ OMWWs are distributed in spring since humidity and temperature conditions favour the biological activity of the soil

◆ OMWWs are distributed 45 days before sowing with regards to herbaceous crops favouring aerobiosis conditions through soil tillage

◆ OMWWs are distributed during autumn-winter before plant recovery with regards to tree crops

◆ a specific fertilization plan has been set up, which takes into consideration the nutrient inputs provided by OMWs as well as soil's physicochemical properties.

For olive husks, in specific, it has to be said that, since they are solid, they are more difficult to spread in such a way so that to be incorporated in the soil system optimally. Neither positive nor negative effects are normally observed on soil properties and/or on crop production when husk amounts **between 20 and 40 tons/ha** are used in relevant field trials e.g. in vineyards and tomato crops. The absence of effects is probably due to the low quantity of olive pomace distributed and to the low degradation rate with a consequent delayed fertilizing effect.

Due to the complexity of the "soil system" and its interrelation with the spread of OMWW it is very important to rely on a monitoring system which could allow a correct evaluation of soil properties and relevant constraints related to OMWW application.

In order to ensure safe disposal of OMW, soil and land data have to be considered in combination with bioclimatic conditions and management practices. The ultimate goal should be to apply or dispose OMW to land in such a way, that the soil either filters the potential toxic elements effectively, or electrochemically absorbs them or decomposes them in order that a clean solution passes through the soil body.

The soil should not be overloaded with inorganic constituents.

Soil must maintain all its functions and its absorption capacity to ensure a sustainable system.

The Soil Monitoring Tool developed within the framework of PROSODOL project is a simple tool for farmers and mills' owners that assists them to monitor soil quality and potential threats for soil by themselves

Technical and economical evaluation of irrigation systems in olive orchard

Approximately 90% of the world olive trees cultivation is located in the Mediterranean basin. This area is characterized by: an average yearly rainfall often lower than 400 mm, a fall-winter season when olive trees receive about 70% of the water and a very dry summer. Therefore, the water deficit is one prevalent environmental factor which affects olive production.

Olive trees can grow in such dry areas, nevertheless it is important to provide a sufficient amount of water during specific phases of its vegetative cycle: especially in spring (flowering and fruit set) and in summer (fruit growing and stone hardening). Especially in young olive orchards, water supply can induce a faster growth, an early production start, the formation of longer shoots that guarantee a higher number of buds and flowers per surface unit and can generally increase fruit set.

Other benefits deriving from the set up of a watering system are: reduction in yield variation (recent studies have demonstrated that with good water supply together with correct fertilization olive trees can produce every year instead of in alternate years), increase in average yield, possibility to reduce pruning, narrowing of plant layout, possibility to grow grass in between rows.

Water supply can be beneficial even for adult olive trees (around 70 years) positively influencing fruit dimension and yield as well as the quantity of oil produced

On the other hand, water deficiencies may induce fruit fall, often anticipated by wilts and browning of fruit, together with a reduction in Potassium (K) assimilation.

Irrigation has relevant effects even on oil quality

Irrigation does not significantly affect free acidity, number of peroxides and spectrometric indexes, which altogether represent the analytical parameters defining an extra-virgin olive oil,

HOWEVER

irrigation can modify the concentration of volatile compounds and polyphenols, which the human nose perceives as e.g. **“fruity”** and **“grassy”.**

Therefore, irrigation can positively modify some oil properties and allow the modification of its analytic, organoleptic and sensorial profile. Water supply according to a so called “controlled deficit” may represent a tool for high quality production (with specific oil aromatic profiles) and it allows water saving in the order of 50% as compared to full watering.

Excessive water supply can lead to excessive vegetative vigour that rebounds on pruning needs to balance the plant and on a variation of organoleptic characteristics of fruit and oil

It is evident that irrigation means also extra costs in terms of design, set up and management of the system in comparison to an olive orchard without any irrigation system. It is also crucial to evaluate costs due to the exploitation of water in areas where it is often shortage.

◆ Field trials carried out in several countries have proved the advantages deriving from irrigation in terms of olive and oil production.

◆ The increase in olive production can reach 100% in comparison to non-irrigated orchards but the extent of the increase depends on soil and climate conditions, olive tree variety, plant lay out and cultivation practices.

Normally, irrigation increases yields in areas where drought periods last for more than 2 months, ETP (potential evapotranspiration) is higher than 1.100 mm per year and rainfall lower than 700 mm.

Considering the above mentioned advantages deriving from the irrigation of olive orchards, the possibility to use wastewaters coming from the agricultural sector - and specifically from the olive sector - for irrigation can represent an opportunity to increase water supply and contribute to water resources conservation.

In Andalusia, an increase between 50-100% in olive yield was registered in irrigated olive orchards (the lower rate at 300 plants/ha; the higher rate at 100 plants/ha).

Set up of an irrigation system using OMWW

When designing an irrigation system it is necessary to evaluate the followings:

◆ age of plants
◆ soil disposition (plane or hill)
◆ plant lay-out and row orientation
◆ soil physical and chemical parameters
◆ available water resources (also alternative resources such as canals, well...)
◆ water physical and chemical parameters

The above are essential in order to define the appropriate water filtration technique, to de-cide whether the olive orchard will be watered entirely or it should be divided in sub-units, to evaluate the possibility to automate the water distribution system or the adoption of other cultivation practices (e.g. pruning, harvesting).

Irrigation system design: structure and sizing

Different watering systems can be set up:

◆ Drip line hanging on the soil surface
◆ Dripper plugged into the watering tube
◆ Sprinklers for micro-dispersion (e.g. on centuries-old plants)
◆ Buried drip line at 20-30 cm depth (subirrigation with anti-siphon technology)

Advantages and disadvantages of the different irrigation systems

Irrigation System	Advantages	Disadvantages
Drip line-drippers	• simple and quick-to-install	• possibly non-homogeneous water supply, especially in case of strong wind. In order to overcome such problems in areas characterized by strong wind high flow is normally used to compensate waterwaste • it can constitute a hindrance to mechanized olive tree operations and processing
Sprinklers	• a plentiful distribution of the water on the soil which is demanded especially for centuries-old plants	• it favors weed growth (which compete with olive trees) and pathogens attack on the surfaces in contact with water, with consequent need for control of plant disease and weeds • it obstructs soil tillage and mechanized harvesting of olives
Sub-irrigation	• even distribution of water • it does not interfere with soil tillage and mechanized harvesting • it is the most efficient irrigation system (90-95% of efficiency in contrast to 50-60% of more traditional methods) • does not disturb or destroy soil structure, reducing the need for soil tillage • it allows a better control of weeds since it does not wet olive leaves directly • it contributes to soil grassing reducing water competition	• tricky installation • high costs related to the early investment • not all kinds of soils are suitable for such system

Irrigation system design: critical aspects

When installing an irrigation system, the following critical aspects should be taken in consideration:

Availability of water: it depends mainly on the presence of wells or canals.

Quality of water: it is crucial for the proper operation of the irrigation system, for its maintenance and for assuring a high uniformity of water distribution.

Filtration system: each installation should be provided with a suitable filtration system in order to retain organic and inorganic particles for an overall correct working of the entire system. Such an aspect is even more crucial when OMWW are distributed because of their lipidic nature and of the presence of suspended particles.

Maintenance of the irrigation system: in the case of hanging driplines, driplines laying on the soil and sprinklers, troubles and obstructions are easily detectable. With regards to subirrigation, besides a precautionary maintenance, it is necessary to verify the correct operation and the flow of the system through water counters. Moreover, it is highly advisable to wash tubes with diluted acid solutions in the beginning of season to guarantee higher duration and efficiency of the system.

Economical aspects related to watering systems

Choice regarding the different possible technical solutions to be installed in an olive orchard depends on the investment the user is ready to undertake.

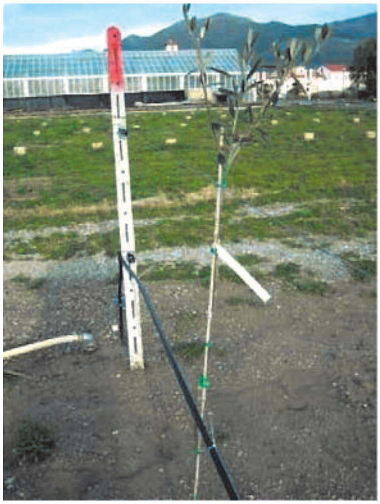
Costs related to the materials depend on many factors (technical, technological and agronomic) - e.g. spacing between rows affects the quantity of dripline used, the quality of the water affects the filtation system needed - so that it is not easy to define general cost assessment rules.

Indicatively,
dripline is cheaper then sprinklers and both of them are cheaper than a subirrigation system.
Subirrigation systems involve high installation costs and elaborate maintenance

Dripline irrigation system-an example

In the following, an example for the installation of a dripline for irrigation and OMWW distribution **in a pilot area of about 2000m²** (i.e. a case study) is presented and explained. The OMWWs, prior distribution and after collection from a 3-phase mill were stored in a plastic container.

The pilot area was provided with a hanging dripline system at 50 cm above soil surface per each olive row. Uniram (Netafim, Israel) pressure compensated tubes, normally used in the agricultural sector for the distribution of water or the application of liquid fumigants, were used.



Such driplines have the following properties:

◆ flow: 2 l/h, ◆ distance between drips: 30 cm, ◆ working pressure: 1,5 bar

Each plant was provided with 2 drips alligned with plant row roughly at 15 cm apart from olive stem. Driplines were fastened to iron wires. Two orders of iron wires were tightened between concrete poles, one to give support to dripline, the other one to give support to plants.
Distance between poles was 10 m.

The area is provided with buried plastic tubes which feed the driplines and are connected to the pump for OMWW distribution.

Filtration

Filtration represented ***the key issue*** during OMWW distribution through dripline, because of the type and the composition of this type of waste.

Ease of distribution can vary depending on the density and the presence of suspended sol-ids in OMWW. Such parameters may present a very high variability during the olive season related to the characteristics of olive milled.

At the pilot field, filtration is realized using simple net filter of 1 inch (other filters that can be used are presented in the following Table, as well). Notwithstanding, a significant re-duction in workability is related to the set up of a filtration system between the feeding tank and the dripline.

It is therefore **highly advisable to adopt a filtration system before OMWW collection in the plastic container in order to have OMWW feeding the dripline with the lowest possible suspended solids content.**

Such a filtration system should consist of steel-made superimposed filtering elements, which should be fed from the top part of the storage tank. Sediments and solids which ac-cumulate within the filter can then be disposed on the soil after appropriate treatment e.g. well mixed with olive husks in order not to create too concentrated hot spots that could be harmful when kept in contact with soil for a prolonged time period.

In case of OMWW characterized by a significant presence of suspended solids, in order to improve workability, one could also consider a different distribution system based on dripline provided **with "sip" drippers**. In this case, dripline is very similar to the one used in the pilot area but water / OMWW dispensers are characterized by higher flows and a distribution mechanism that does not include an ad hoc winding water path like inside pressure compensated driplines.

Materials for the set up of a complete irrigation system and relative costs

Item	Specific	Cost	m.u.
Dripline	Pressure compensated Flow: 1,5 – 2 l/h	0.30 – 0.60	€/m
Concrete poles		2.50 – 3.50	€/each
Iron wires		1.50 – 2.00	€/m
Wire tightener		1.50 – 2.00	€/each
Solenoid valve		65.00– 70.00	€/each
Tubes	Polyethylene ∅ 16 mm (between feeding tube and dripline)	0.42	€/m
	Trichoflex ∅ 40 mm Trichoflex ∅ 50 mm (to connect buried PE tubes among plots)	1.20 1.80	€/m €/m
	PE tubes ∅ 40 mm PE tubes ∅ 50 mm (buried)	1.90 2.80	€/m €/m
Pump	750 W	150-250	€
Joints	PE valves	2.00	€/each
	PE L tube	0.20	€/each
	Cork ∅ 40 mm Cork ∅ 50 mm	4.80 7.00	€/each €/each
	Sleeve coupling	0.16	€/each
	Spheric valve 1" ¼ Spheric valve 1" 1/2	26.00 38.00	€/each €/each
	Fast coupling 1" ¼ Fast coupling 1" 1/2	5.00 6.00	€/each €/each
	PE joint 1" ¼ PE joint 1" 1/2	5.30 6.80	€/each €/each
	Clamp joint ∅ 40 mm Clamp joint ∅ 50 mm	2.20 2.30	€/each €/each
	Tap (between clamp joint and dripline)	1.50 – 1.80	€/each
Filters	Net – 1" Net - 1,5"	30.00 .40.00	€/each €/each
	Bag filter (steel) Filtering bags	1,635.00 12.00	€/each €/each
	Disc filter (Azud type) ∅ 1 inch	20.00 – 50.00	€/each

The distribution of OMWs on soil must always satisfy restrictions set by national and European laws. However, since OMWs could be considered as fertilizing materials that can be used in the agronomic sector, apart from the highest values set by law and in order to ensure sustainability, if you plan to distribute OMWs on soil, then the annual distribution rate and timing of wastes application should be determined, regardless if wastewater or solid OMW (i.e. dry husk, wet husk, composts from all mills by-products), or wastes originated from two-phase systems are to be distributed. This means that it could be possible to use smaller amounts of OMW on your land than those set by law, because the soil of your land and the local conditions do not permit such amounts and lower OMW amounts could ensure the good quality of your land.

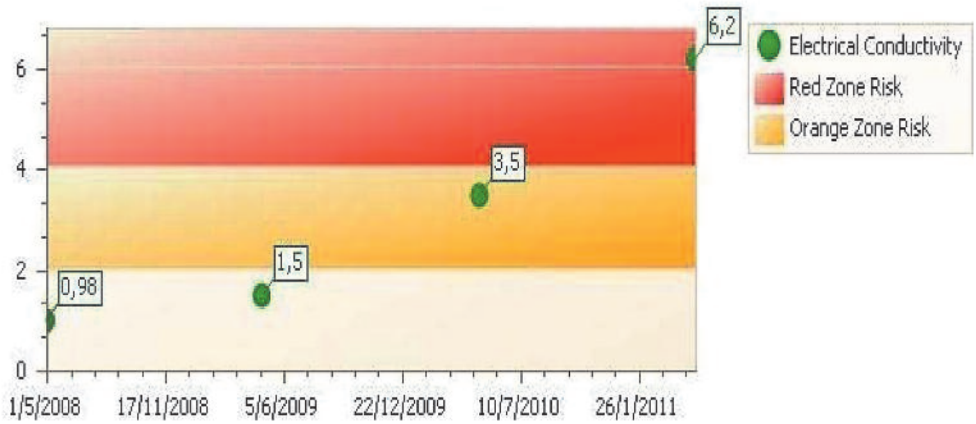
The annual distribution rate should be estimated after evaluation of the specific local environmental conditions and soil quality. Since the most of the OMW constituents are non-toxic and are considered as important nutrients (nitrogen, phosphorous, potassium, organic matter, iron, etc), the application of OMW could be beneficial for soil quality and may improve fertility. However, due to the very high load of OMW in these constituents, the disposal on soil should follow restrictions and rules and the annual application should be estimated by considering:

- The natural concentration of the specific elements/substances in soil
- The concentration of the specific elements/substances in OMW
- The specific climatic, geomorphologic and environmental conditions of the area that may affect the behavior of these elements/substance in soil (leaching, adsorption, decomposition, etc)
- The maximum permitted amount of each of these elements/substances that can be disposed on soil without changing its quality
- The thresholds of each soil parameter as defined in national and European laws and also derived from the literature, especially for the non-toxic macronutrients (e.g. Phosphorous, Nitrogen,etc) and for the available forms of metals (Table of Annex 2).

Thus,

For safe reuse or safe disposal of OMW on soil, specific care should be taken and the decisions should be taken only after detailed evaluation of all potential risks for soil and the environment

In order to efficient and safely use OMW on soil and in order to estimate the annual distribution rate correctly, it is strongly recommended to ask your agronomist or other expert for advice and technical assistance



SOIL DISPOSAL – MONITORING SOIL QUALITY

Regardless of the purpose (e.g. discharge, irrigation, fertilization), the disposal of Olive Mill Wastes on soil may cause serious problems and significant degradation of its properties and thus to its functions.

Detailed and accurate studies performed so far, revealed that almost all organic and inorganic soil constitutents are increased due to wastes disposal. If the disposal is continued for a long time interval, then **soil is threatened by permanent degradation, which is irreversible.** Thus, it is very important to monitor soil quality periodically (at least once every two years) and record changes. It would be also very useful to keep an updated inventory with the results of the chemical analyses, so that to be able to compare recent results with older ones. By this comparison it would be easier to define potential risks and increased trends in soil parameters' values. An example of a periodical monitoring of soil Electrical Conductivity is seen in the following graphical representation.

In the lab, a soil sample is typically analyzed for: Texture, (clay, silt, sand), pH, $CaCO_3$, Saturation Percentage, Organic Matter, Total Nitrogen, Available Phosphorous and Boron, Exchangeable K, Ca, Mg, Na, Water Soluble Na, Cation Exchange Capacity, Available Fe, Cu, Mn, Zn, NO_3^-, SO_4^{2-}, NH_4^+, PO_4^{3-}, Cl^-, Polyphenols and Heavy Metals.

After extensive soil survey and periodical monitoring of many OMW disposal areas, the most suitable soil parameters (i.e. **soil indicators**) which describe the quality of soils that accept the disposal of mills wastes and which should be monitored periodically were identified during PROSODOL project implementation.

Thus, instead of measuring all soil parameters in order to monitor a disposal area periodicaly, **you have to measure only the following eight Soil Indicators.**

Soil Indicators

Organic Matter
Polyphenols
Electrical Conductivity
Total Nitrogen
Available Phosphorous
Exchangeable Potassium
Available Iron
pH

Use the monitoring tool for mills' owners. Install the tool in your PC and monitor the quality of your land periodically by yourelf.

Soil color and texture could be also used as additional indicators and should be continuously monitored.

Observe changes in soil color and cohesion of soil aggregates
Ask for advice in case of unexplained and persisted changes

Soil sampling and application of the Monitoring Tool

Soil quality should be monitored periodically, ideally annually or at least once every two years. For this, choose appropriate areas within your property, which are permanently affected by the disposal of mill wastes, **directly** and **indirectly.**

Indirectly affected areas are those that are affected by the wastes' disposal mainly by wastes leaching through soil, although they do not accept direct disposal. Such areas could be found, for example, at sloped areas near disposal ponds. See an example on how to recognize indirectly affected areas in the following photo.

Directly affected areas are those that accept surface wastes disposal

The specific disposal area includes two wastes disposal ponds. The areas downsream of the two ponds as well as the area between the two ponds are indirectly affected areas.

To monitor soil quality of your land, the following steps will help you:

Step 1: Observe and identify which areas are directly or indirectly affected by the wastes, considering specific soil properties such as slope, texture and color, as well as other areas that you believe you should monitor. Identify clean areas and use them as control areas.

Step 2: Categorize the areas and decide from which of them you will collect samples. You may need to ask for the contribution of an expert (agronomist, environmentalist) to help you with the selection of the appropriate sampling sites. In any case you should collect samples from directly and indirectly affected areas as well as samples from clean areas (i.e. "background" or "control" samples) so that to compare the results.

Step 3: After selection of the appropriate sampling sites, you should proceed with samples collection.

Step 4: You should collect surface samples (0-25cm) but also samples from deeper soil layers (25-50cm, 50-75cm, 75-100cm). Use appropriate instruments for digging and sample collection (Annex 3). Remember to follow exactly the same procedure for the control samples and to collect samples the same season each year.

Step 5: Transfer the collected samples to a chemical laboratory as soon as possible to ensure no changes in the physicochemical properties of the soil samples and especially of polyphens content and pH.

Guidelines for soil sampling you may found in Annex 3

Step 6: Analyse soil samples for pH, electrical conductivity, organic matter, polyphenols, total nitrogen, available phosphorous, exchangeable potassium and available iron.

Step 7: Create an inventory by inserting the results in the monitoring tool which you can download from PROSODOL project web site and install on a PC. In a different case, you may ask your agronomist or consultant to create an inventory for your area. You can create eight different graphs for each one of the soil indicators.

See an example of the application of the monitoring tool and indicative graphs for the eight soil indicators in Annex 4

Threshold values for the eight Soil Indicators

Soil Indicator	Normal	High-Very high	Excessive
Organic Matter, %	3.4-5.0	(h.t.) 5.0	
Polyphenols, mg/kg	(l.t.) 40		
Electrical Conductivity, mS/cm	(l.t.) 2.0	2.0 – 4.0	(h.t.) 4.0
Total Nitrogen, %	(l.t.) 0.3	(h.t.) 0.3	
Available Phosphorous, mg/kg	12-28	40-50	
Exchangeable Potassium, cmol/kg	(l.t.) 1.2	1.2-2.2	(h.t.) 2.2
Available Iron, mg/kg	(l.t.) 50	50-100	(h.t.) 100
pH	6-8		

(l.t.): lower than; (h.t.) : higher than

By inserting the values of the soil parameters in the respective page of the software, the system will automatically recognize the values and inform you, by using a color scale, if these value are acceptable, close to risk, or risky.

COMPOSTING OLIVE MILL WASTES

Composting is the most commonly used method applied for the recycling and transformation of organic wastes into fertilizers-soil amendments. In the case of OMWs, it is possible to mix directly with manure from seep, cattle, horse, chicken or other suitable Nitrogen sources, as well as with other raw materials such as straw, leaves, prunings, etc.

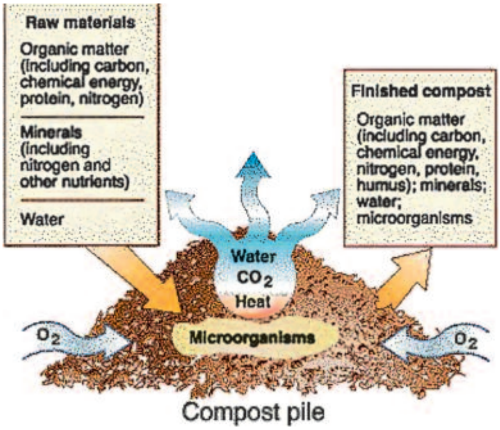
What is composting?

Composting is a controlled aerobic and thermophilic decomposition, the natural breakdown process of organic residues. Composting transforms raw organic waste materials into biologically stable, humic substances that make excellent soil amendments. Compost is easier to handle than manure and other raw organic materials, stores well and is odor-free, while the high temperatures reached during the process ensure the sanitization of the final product.

Composting is a natural breakdown process of organic residues

Composting is an ancient technology, practiced today at every scale from the back-yard compost pile to large commercial operations

Typical mixing ratios for composting OMWs vary from 50 to 75% of OMW and 25-50% of a Nitrogen resource such as manure. Urea can be added to increase the Nitrogen content of the starting mixture to achieve an initial Carbon to Nitrogen (C/N) ratio close to 25-30.



Olive tree prunings can be also used as bulking agent to improve the physical texture and aeration of the pile.

Examples of mixing OMWs with other agricultural wastes

Mix:
40% TPOMW
40% Chicken Manure
20% Straw and leaves
Production cost
0.05-0.06 €/kg compost

Composting using widrows in Spain

Composting using different source materials in Portugal

Mix:
70% OMW from 3-phase mill
10% wheat straw
10% chicken manure
10% olive pruning

Mix:
45% OMW
45% goat manure
10% grape stalks

Co-composting of OMW (EL.VA Ltd., Bambakopoulo, Chania, Crete, Greece)

Uses and markets for compost

As landfills reach their capacity and ban acceptance of organic wastes, composting is an increasingly viable means of organic waste management. Most importantly, the final product is a **valuable soil resource.** Compost can replace materials like peat and topsoil as seed starters, soil amendments, mulches and natural fertilizers in commercial greenhouse production, farms, turf and land remediation.

There is a big potential demand for compost in plant production-related industries—close to 900 million cubic yards of compost could be used in agricultural and horticultural applications and 0.6 million cubic yards for land fill covers and surface mine remediation.

Benefits of adding compost to soils

Compost is an organic matter source with a unique ability to improve the chemical, physical, and biological characteristics of soils. It improves water retention in sandy soils and promotes soil structure in clayey soils by increasing the stability of soil aggregates.

Soil becomes microbially active and more suppressive to soil-borne and foliar pathogens. Enhanced microbial activity also accelerates the breakdown of pesticides and other synthetic organic compounds. Compost amendments reduce the bioavailability of heavy metals—an important quality in the remediation of contaminated soils.

Adding compost to soil increases soil fertility and Cation Exchange Capacity and can reduce fertilizer requirements up to 50%

Compost application

Composting OMW (A. Patrinos & Son, Katastari Zakynthos, Greece)

SOIL REMEDIATION

On 22 September 2006 the European Commission adopted a **Soil Thematic Strategy** (COM(2006) 231) and a proposal for a **Soil Framework Directive** (COM(2006) 232) with the objective to protect soils across the European Union. Within this framework, the EU Member States will be in a position to decide how best to protect soil and how use it in a sustainable way on their own territory.

The overall objective is protection and sustainable use of soil, based on the following guiding principles:

- preventing further soil degradation and preserving its functions
- when soil is used and its functions are exploited, action has to be taken on soil use and management patterns
- when soil acts as a sink/receptor of the effects of human activities or environmental phenomena, action has to be taken at source
- restoring degraded soils to a level of functionality consistent at least with current and intended use, thus also considering the cost implications of the restoration of soil

So far, no specific technique has been developed for soil remediation at OMW disposal areas

In the framework of PROSODOL project, two methods were developed and implemented in a pilot area in Crete Island, South Greece. The evaluation of the results revealed that both of them are suitable for OMW disposal areas, if applied properly and under scientific and technical control by qualified persons. These techniques are (a) **bioremediation** and (b) **application on soil of the natural zeolite, namely clinoptilolite.**

The two techniques target to different soil properties and contaminants and their application depends on the specific problem recorded at the targeted areas. Thus, bioremediation targets to organic pollutants, such as polyphenols, while the application of zeolite targets to the inorganic soil constituents. Considering these, **it is very likely to apply both techniques at the same waste disposal area, however, starting from bioremediation.**

Member States should systematically identify damaged soils, combat soil degradation and identify areas where there is a risk for soil and then adopt risk reduction and remediation plans for affected areas, within national remediation strategies

Bioremediation

Uncontrolled discharge of olive mill wastes directly on soil may impact soil physical and chemical properties. Soil pollution and consequently the high risk of groundwater pollution are worldwide problems that may result in uptake and accumulation of toxic chemicals in food chains and also harm flora and fauna of affected areas.

Bioremediation is a process in which microorganisms metabolize contaminants either through oxidative or reductive processes. As such, it uses relatively low-cost and simple techniques, which generally have high public acceptance and can often be carried out on site.

However, bioremediation is not always suitable since the range of contaminants on which it is effective is limited; the time scales involved are relatively long; and the residual contaminant levels after its implementation may not always be acceptable. Under favourable conditions, microorganisms can completely oxidize organic contaminants and convert them into non-toxic by-products such as carbon dioxide and water or organic acids and methane.

Principles of Bioremediation

Bioremediation is a process whereby organic wastes are biologically degraded under controlled conditions to an innocuous state, or to levels below concentration limits established by regulatory authorities. It uses naturally occurring bacteria and fungi or plants to degrade or detoxify substances that are hazardous to human health and/or environment.

The microorganisms may be indigenous to a contaminated area or they may be isolated from elsewhere and brought to the contaminated site.

Bioremediation targets to the biological degradation of polyphenols, which are considered the most toxic constituents of the OMWs

Contaminants are transformed by living organisms through reactions that take place as a part of their metabolic processes. Bioremediation process refers to the enhancement of this natural process,

- either by adding microorganisms to soil, referred to as bioaugmentation,
- or by providing the appropriate conditions and/or amendments, such as supplying oxygen, moisture and nutrients, to enhance microorganisms growth in soil, referred to as biostimulation.

Bioremediation **in the presence of air or oxygen is called aerobic bioremediation** and typically proceeds through oxidative processes to render the contaminant (polyphenols) either partially oxidized to less toxic by-products or fully oxidized to mineral constituents, i.e. carbon dioxide and water.

Bioremediation can be implemented directly on polluted soil (in-situ bioremediation), or by removing and transferring soil to a specifically dedicated area for treatment (ex-situ bioremediation)

Under **anaerobic conditions**, bioremediation processes are more complex. In anaerobic respiration, organic contaminants can be mineralized provided that sufficient nitrate or sulphates are present. Typically, aerobic bioremediation is faster than anaerobic bioremediation; therefore, it is often preferred.

At many contaminated sites there exist microorganisms that have developed the capability to naturally degrade the present contaminants.

However, not all sites are enriched in suitable microorganisms and typically the lack of appropriate environmental conditions inhibits rapid contaminants degradation. In such cases, Engineered bioremediation, typically involves oxygen supply, moisture, and nutrients to the contaminated soil zone so that, to stimulate contaminants degradation by the naturally existing microorganisms. In order degradation to be satisfactory occurred it has to be ensured that oxygen (or air), moisture and nutrient concentrations are maintained in sufficient levels and at the proper rate. This requires extensive monitoring to assure that the process is proceeding satisfactorily.

The monitoring can be performed by maintaining monitoring wells and also by measuring the concentrations of carbon dioxide and other substances that are produced during bioremediation precess called metabolites. The increase in biological activity is also a parameter that should be monitored by measuring the decrease in oxygen concentration (for aerobic processes) or by the build-up of metabolites (e.g. ethene from the reductive dechlorination of tetrachloroethene).

Advantages

Bioremediation is a natural process and is perceived by the society as an acceptable waste treatment for contaminated soil

It may result in complete degradation of organic compounds to non-toxic by-products and includes carbon dioxide, water and cell biomass

A wide variety of compounds that are legally considered to be hazardous can be biodegraded to harmless products

There are minimum mechanical equipment requirements

It can be implemented as in-situ or ex-situ process. In-situ bioremediation is safer since it does not require excavation of contaminated soils and does not disturb the natural site surroundings

It is a low cost technique as compared to other remediation technologies.

Disadvantages

There is a possibility for partial degradation of pollutants to metabolites that are still toxic and/or potentially of higher mobility

As a biological process is often highly specific and sensitive to toxins and environmental conditions

A detailed study is needed in order to develop and engineer bioremediation application to sites with mixtures of contaminants

Extensive monitoring is required to determine biodegradation rates and overall progress

It may be difficult to control volatile organic compounds produced during ex-situ bioremediation process

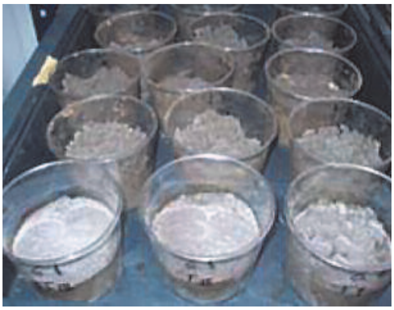
Generally requires longer treatment time as compared to other remediation technologies

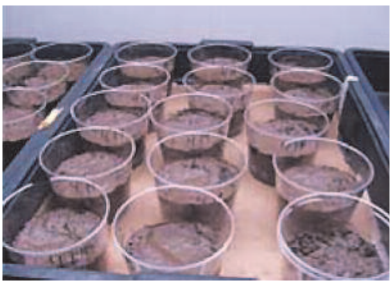
It is difficult to extrapolate from bench and pilot-scale studies to full-scale field operations

Bioremediation can be used in any soil type with adequate moisture content, although it is difficult to supply oxygen and nutrients into low permeability soils.

Very high concentrations of polyphenols may be toxic to microorganisms and thus may inhibit their activity. In such cases of heavy contaminated sites bioremediation may not be the best remediation option.

Therefore, prior implementation, a **feasibility investigation** is needed to determine if biodegradation is a viable option for the specific site, soil type and contaminant conditions.





Lab feasibility experiments

What you should know before you decide to apply the method

◆ An adequate site characterization, including surface soil characteristics, subsurface hydrology, and microbiological characteristics, is the basis for the rational design of a bioremediation system.

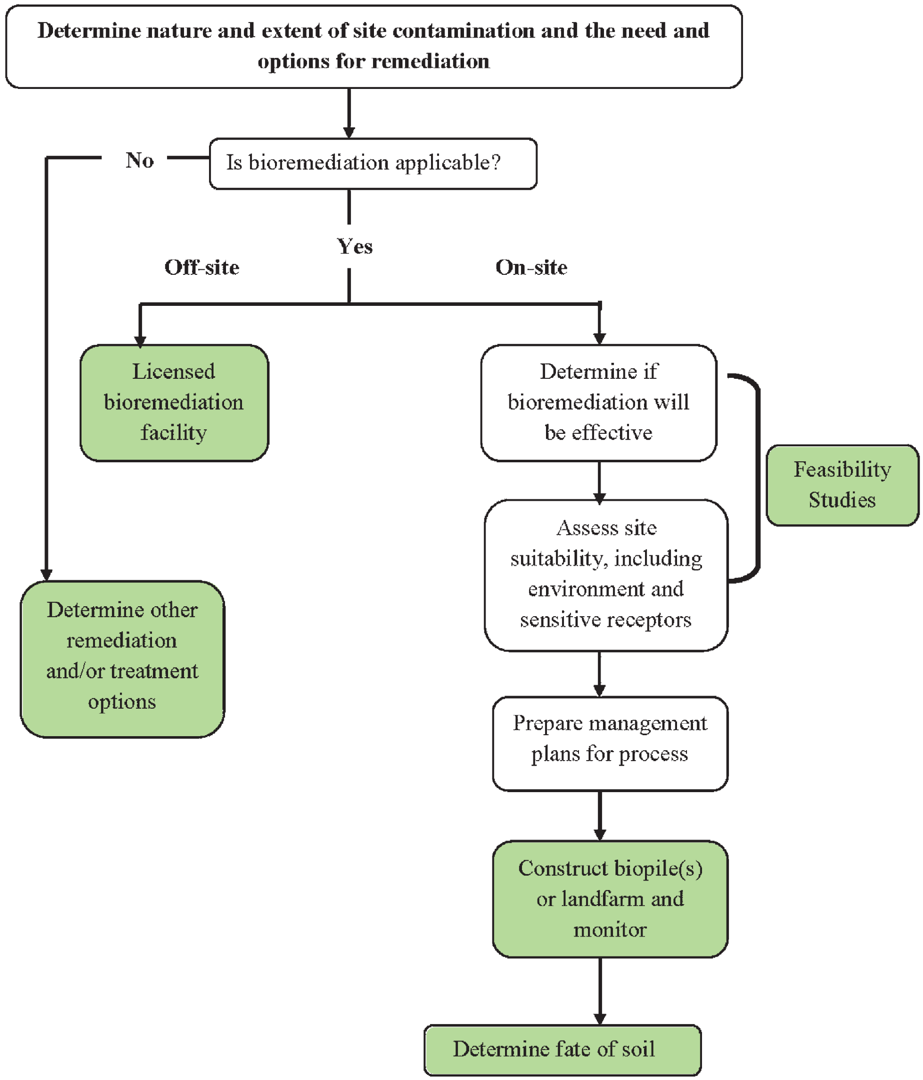
◆ Microbiological characterization of a contaminated site should be conducted to ensure that the site has a viable community of microorganisms to accomplish biodegradation of the organic pollutant present at the site. Approach to estimating the kinds, size and metabolic activities of soil microbial population are very common.

◆ Specifically for olive mill wastes, it is very important to establish the environmental factors (water, oxygen and nutrients content, pH, and temperature) that can be critical for the microbial biodegradation of polyphenols because the management of bioremediation is strongly depended on the nature and concentration of chemical substances, as well as the proximity of the bioremediation process to sensitive environments and human activities.

◆ Several national environmental agencies (European Agency, US-EPA, Australian EPA) consider that any proposal for bioremediation should demonstrate adequate safeguards for the protection of human health and the environment. Considerations include the control, minimisation and monitoring of emissions or discharges from the bioremediation process.

◆ Prior the implementation and in order to ensure the feasibility of this technique is necessary to study in laboratory (feasibility study) which is the more suitable soil treatment/management in order to increase the bioaugmentation and biostimulation of soil microbial community and to monitor in these conditions the risk of phytoxicity or ecotoxicity as well as, the polyphenols concentration through soil incubation.

A flowchart outlining the strategy involved in bioremediation activities is provided in the following diagramm.



Flowchart outlining the strategy involved in bioremediation activities

Bioremediation laboratory tests are necessary to be performed while the evaluation of the results will allow:

i) to confirm that the polyphenols are available to microorganism and can be biodegraded.

ii) to observe that polyphenols biodegradation will be relatively fast.

iii) to confirm that soil aeration (oxygen content improvement) increases polyphenols biodegradation rate in controlled conditions (water content, temperature and pH).

iv) to identify the role of nutrients addition (especially Nitrogen and Phosphorous).

v) to identify the potential positive effect of the addition of other materials, such as composts, humic extract of composts.

Prior the bioremediation implementation at the selected area, the following issues should be also clarified:

i) history of the area (e.g. previous soil uses and amendments, frequency and amount of wastes disposed, etc), present and future use, as well as geomorphological and hydrological data.

ii) physicochemical characteristics of the disposed olive mill wastes obtained through physicochemical analysis.

This information combined with the result obtained from laboratory studies would assist the selection of the most suitable method for the bioremediation of degraded soils due to OMW disposal.

For the successful implementation it is important to avoid further wastes disposal at the area and thus protection of the area under treatment with a physical or technical barrier is considered important and necessary.

In case that your land accepts disposal of olive mill wastes, it is recommended to consider the implementation of a soil remedial technique. Experts and scientists could help you to implement the selected technique.

In order to monitor the bioremediation progress, periodical soil sampling (every 15 days during the first month) and samples analysis was also suggested. After the first month longer sampling periods could be adopted (every 30 days).

Additonally, polyphenols content should be also monitored periodically.

Because olive mill wastes disposal on soils cause not only an increase in polyphenolic compounds, but also could cause substantial changes in many physicochemical soil properties, such as inorganic elements content, electrical conductivity and pH, it is recommended to monitor also some soil microbial parameters, such as microbial biomass; microbial respiration and dehydrogenase. These parameters are important for the determination of the evolution of the microorganism activity extent while, from the other hand the physicochemical parameters are important for the further identification of soil quality and health. For this fact, it is necessary to monitor the evolution of all these parameters during a bioremediation treatment.

Additionally, the determination of polyphenols content in deeper soil horizons would be interesting and may offer useful conclusions.

THEREFORE
a specific programm for monitoring your area should be developed with the assistance of experts

Natural Zeolite as soil amendment

Natural zeolites are minerals with unique properties, owed mainly to their structural characteristics, i.e. their three-dimensional structure which contains regular channels and cavities (like honeycomb) of sizes similar to those of small to medium-sized molecules (see figure below). As such, they are ideal molecular sieves, have high level of selectivity which could be exploited in catalysis and ion-exchange. In many zeolites these frameworks are open, so cations and water molecules, contained in cavities and channels within the frameworks, have freedom of movement.

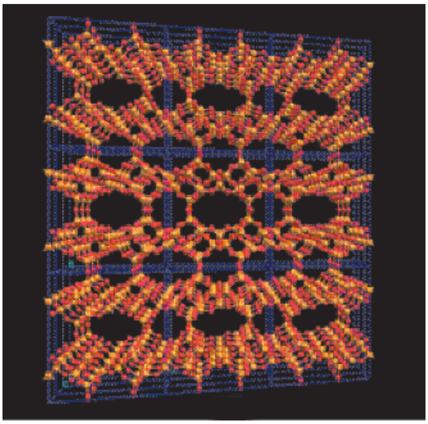
The unique structure of channels, cavities and cages results in large internal surface available for a variety of reactions, and it is this surface that controls most of the useful properties of zeolites.

Zeolites have often been characterized as sponges with large internal surface available for use

World production of natural zeolites 2.5 – 3.0 Mt

DEPOSITS

China	Bulgaria
Korea	Australia
Japan	New Zealand
USA	Georgia
Indonesia	Philippines
Turkey	Slovakia
Hungary	Canada
South Africa	Greece
Cuba	Italy



Honeycomb structure inside which many species (ions, charged groups and small molecules) can be retained

Clinoptilolite cost depends on grain size and varies between 40€ and 175€ per ton

Clinoptilolite

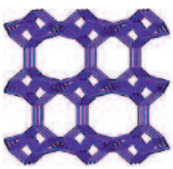
Clinoptilolite is one of the most abundant natural zeolite.

- ✓ **Clinoptilolite doesn't break down over time**
- ✓ **Remains in soil and improves nutrient retention**

IN SOIL

- ✓ **Reduces irrigation need**
- ✓ **Reduces fertilizers input**
- ✓ **Retains beneficial nutrients in root zone**
- ✓ **Improves aeration**
- ✓ **Assists buffering in case of acidic soils**

Clinoptilolite has numerous uses and benefits in maintaining and improving the quality of air, water, solid wastes and wastewaters. Similarly as other natural zeolites, clinoptilolite has been widely studied regarding its suitability to be used in many different environmental applications worldwide, including protection, improvement and also remediation of soil quality.



How to apply Clinoptilolite on soil at OMW disposal areas

✓ Prior the application, preliminary land configuration activities should be carried out. In particular, the disposal area should be homogenized with the use of field machines (e.g. tilling machines, excavators, mechanical shovel) up to almost 25cm soil depth. Stones should be preferably removed.

✓ The addition of clinoptilolite at 5% w/w is considered appropriate for OMW disposal areas considering that no further OMW disposal will occur. To achieve 5% zeolite in soil, add almost 150ton of clinoptilolite per hectare.

✓ It is recommended that clinoptilolite should be of small grain size in order to be more effective and well distributed. Thus, it could be applied in dust form with particles diameter smaller than 0.8mm, or of slightly larger size (0.8mm-2.5cm). Very small grains size, although more effective, is difficult to be distributed because of the dust produced during the application. However, it may be considered the possibility to use a mixture of of different grain sizes (in dust form and grains size of 0.8mm-2.5cm).

✓ Clinoptilolite should be distributed homogeneously and very well tilled.

✓ After application, it is possible that periodical irrigation, in order to avoid excess sodium leaching would be necessary. The amount of applied water should be defined based on total cumulative net infiltration (subtracted estimated evaporation and adding precipitation), considering water parameters (chemical properties) and soil properties (e.g. soil bulk density, moisture content, electrical conductivity, texture, exchangeable cations). This management intends to achieve high leaching efficiency (i.e. remove the maximum salt possible per unit of leaching water) by using intermittent leaching with continuously unsaturated conditions on the soil surface, minimizing some surface ponding.

SODIUM concentration in soil should be monitored after the application due to the anticipated sodium leaching which could lead to excess sodium concentration in soil

SODIUM remains high for a short period (almost 2 months after application) while after that period very small amounts of sodium are anticipated to be found in soil

Keep in Mind

If you irrigate your land with OMWW (in accordance to the law) it is recommended to add no more than 2% zeolite on soil. This will assist soil (especially soils rich in sand) to retain nutrients and increase cation exchange capacity, properties that are negatively affected by the OMWW acidity

Monitoring soil quality after zeolite application

✓ Soil quality should be monitored annually
✓ Sampling and soil analysis should be carried out following the national and EC regulations
✓ Results should be kept in an inventory and evaluated in order the total improvement or potential problems to be in time recorded and accordingly assessed
✓ Soil samples should be analyzed for the proposed eight soil indicators
✓ Soil should be analyzed also for exchangeable sodium and water soluble sodium. It is recommended to include Sodium Adsorption Ratio (SAR) and Exchangeable Sodium Percentage (ESP) determinations in the regular soil monitoring strategy. Especially, after zeolite application, soil samples should be analyzed for SAR and ESP every two months and for the first six months period after application. In case that values of SAR and ESP exceeded the upper limits (13cmol/kg1/2 for SAR and 15% of ESP) for more than 3 continuous samplings then a contingency plan, which will include periodical soil irrigation, should be put in force.

Anticipated Benefits

Soils that accept uncontrolled disposal of OMWs are often very much degraded and are characterized by very high values of Electrical Conductivity and very high content of Organic Matter, Polyphenols, total Nitrogen, available Phosphorous and Boron, exchangeable Potassium and Magnesium, available

Soil degradation has been proved to be in most of the cases **IRREVERSIBLE**

Iron, Copper, Manganese and Zinc, Nitrates and Sulphates. Morever, there are cases of Nickel and Chromium contamination but only if the stainless steel parts of the mills are of inferior quality (old mills)

Clinoptilolite is anticipated to positively affect

✓ Soil organic matter (OM) content. The use of clinoptilolite as soil amendment is anticipated to stabilize and to maintain soil OM values at constant values. This is owed to the improvement of soil aeration and thus to the enhancement of soil microorganism activity to biodegrade soil organic matter. Soil aeration can be improved by using zeolite of larger grains size (e.g. 0.8-2.5mm).
✓ Total nitrogen. The effect of zeolite on total nitrogen content is similar to that on OM content and due to the same reasons.

✓ Exchangeable potassium and available metals (iron, copper and manganese) are anticipated to be increased in soil. The increase is owed to the retention of these elements from clinoptilolite. However, the increase is not attributed to the increase of these elements in soil particles but in zeolite framework. Consequently, this increase does not lead to extent K, Fe, Mn, Cu leaching but to slow release from zeolite to soil solution contributing thus to the improvement of soil quality and to the prevention of nearby systems overloading.

✓ Soil electrical conductivity (EC), is anticipated to be reduced due to the retention of ions within zeolite framework. Thus, despite the increase in exchangeable potassium and available metals contents in soil, these amounts do not increase soil electrical conductivity because ions are held in/on the zeolite framework.

✓ Soil pH. For acidic soils and low in CaCO3, it is anticipated that the addition of clinoptilolite will enhance the neutralization of OMW's acidity.

On the Contrary

✓ No significant effect is anticipated on polyphenols content, which are the most toxic constituents of OMWs

✓ No significant effect is anticipated on available phosphorous content

✓ No significant effect is anticipated on exchangeable magnesium

Better results could be achieved by the combination of the two methodologies i.e. the Bioremediation and the application of Clinoptilolite

thus

it is anticipated that polyphenols will be decomposed during bioremediation while the zeolite application will ensure the reduction of soil organic matter and total nitrogen from the very high unstable values to lower, normal and constant values, to the reduction of electrical conductivity, while at the same time will control the concentration of potassium and available metals

ANNEXES

Annex 1: Tables with average values of Olive Mill Wastes' properties.

Annex 2: Critical levels and accepted values of some main soil parameters that can be used for the evaluation of soil chemicalanalysis results.

Annex 3: Guidelines for soil sampling.

Annex 4: Examples for the use of PROSODOL monitoring tool

ANNEX 1

Table 1. Average values of the characteristic parameters of olive mill wastes originated by pressure and 3-phase centrifugation systems

Parameter	Pressure System	3-phase system
pH	5.27	5.23
Dry matter, g/l	130	61
Electrical Conductivity, dS/m	18	12
Specific weight	1.049	1.020
Oil, g/l	2.3	5.8
Reducing sugars, g/l	36	16
Total phenols, g/l	6.2	2.7
Ash, g/l	20	6.4
BOD, g O_2/l	68.7	45.5
COD, g O_2/l	146	86
Organic nitrogen, mg/l	544	404
Total phosphorous, mg/l	485	185
Sodium, mg/l	110	36
Potassium, mg/l	2470	950
Calcium, mg/l	162	69
Magnesium, mg/l	194	90
Iron, mg/l	33	14
Copper, mg/l	3.1	1.6
Zinc, mg/l	3.6	2.06
Manganese, mg/l	5.3	1.6

Table 2. Characteristics of olive husks (mean values)

Parameter (%)	Press	3-phase
Moisture	27,2	50,2
Fats and Oils	8,72	3,89
Proteins	4,77	3,43
Total Sugars	1,38	0,99
Cellulose	24,1	17,4
Ash	2,36	1,70
Lignin	14,2	10,2
Kjeldahl Nitrogen	0,71	0,51
Phosphorous (P_2O_5)	0,07	0,05
Total Phenols	1,15	0,33
Potassium (K_2O)	0,54	0,39
Calcium (CaO)	0,61	0,44
Total Carbon	42,9	29,0
C/N ratio	60,8	57,2
C/P ratio	588	553

Table 3. Average values of the characteristic parameters of olive mill wastes originated by two-phase system

Parameter	2-phase system
pH	5.32
Electrical Conductivity, dS/m	3,4
Total phenols, %	1.22
Ash, g/kg	67.4
Organic nitrogen, %	1.14
Total phosphorous, %	1.16
Sodium, g/kg	0.7
Potassium, %	2.00
Calcium, g/kg	4.5
Magnesium, g/kg	1.7
Iron, mg/kg	614
Copper, mg/kg	17
Zinc, mg/kg	21
Manganese, mg/kg	16

ANNEX 2

Critical levels of some main soil properties (Kavvadias et al.,2010)

Soil properties	normal/average range	high	very high	excessive	Comments
pH	6-8				
Electrical Conductivity (EC)	2.0mS/cm			>4.0mS/cm *	* soil quality threshold
Organic Matter (OM)	> 3.4%	> 5%			
Total Nitrogen (N)		> 0.3 %			
Available Phosphorous (P)	12-28mg/kg	40-50mg/kg >33-36mg/kg			
		>59-60mg/kg			
Exchangeable Magnesium (Mg)	1.2-2.2cmol/kg		> 2.2 cmol/kg *		* -Nutrient imbalances due to Mg antagonism -Adverse effect on soil quality
Exchangeable Potassium (K)	0.26-0.60cmol/kg		>1.2cmol/kg	>2.0cmol/kg	
Exchangeable Calcium (Ca)	2.5-3.8cmol/kg		> 20cmol/kg		
Extractable Ammonium (NH_4^+)	28-280mg/l				
Phenols	target value: 0.05mg/kg				< target value: clean soil; < target value < intervention value: slight contaminated soil; > intervention value: contaminated soil
	intervention value 40mg/kg				
Hot water soluble Boron (B)	0.5-1.5 mg/kg	1.6-3.0mg/kg		>3mg/kg	For medium to heavy soils in texture
				>2-3 mg/kg * >5 mg/kg *	* phytotoxicity
Available Copper (DTPA-Cu)		> 3.0mg/kg	1.6-15 mg/dm³	>20mg/kg *	* potential phytotoxicity
Available Iron (DTPA-Fe)			> 50mg/kg	> 100mg/kg	
			25-60mg/dm³		
Available Manganese (DTPA-Mn)			> 50mg/kg		
			10-50mg/dm³		
Available Zinc (DTPA-Zn)			> 8.1 mg/kg⁻¹		
			2.4-15mg/dm³	> 130 mg/dm³	

ANNEX 3

General steps involved in soil sampling

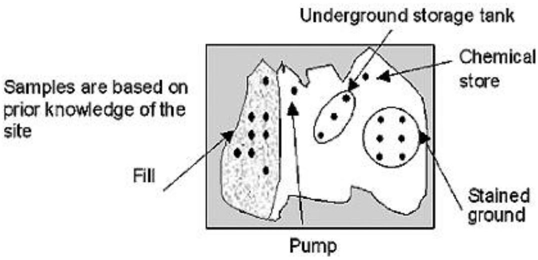
A. Preliminary site investigation

Development of sampling plan

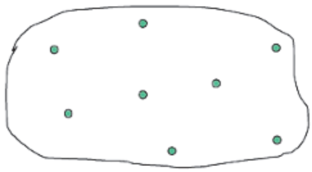
All possible information that is directly or indirectly related to the site to be sampled and the parameters to be measured in the samples should be known or collected collected, e.g. location and history (e.g. maps, soil type, climate); site use; contamination (quality and quantity of the OMW and disposal practices); past environmental Studies.

Selection of sampling approach

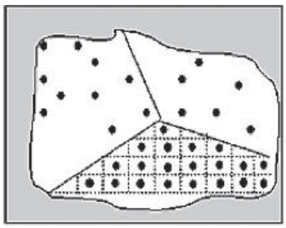
Judgmental sampling is the subjective selection of sampling locations at a site, based on historical information, visual inspection, and on best professional judgement of the sampling team. Judgmental sampling is used to identify contaminants present at areas having highest concentrations. Only use judgemental sampling when there is reliable information about the site (eg, site history, the location of specific areas of concern is known).

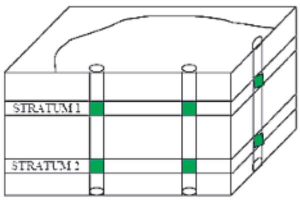


Random sampling is the arbitrary collection of samples within the defined boundaries of the area of concern. The arbitrary selection of sampling points requires each sampling point to be selected independent of the location of all other points, and results in all locations within the area of concern having an equal chance of being selected.



Stratified random sampling covers division of the sampling area into smaller areas called strata. This is done on the basis of historical information and prior analytical results or screening data. Each stratum is more homogeneous than the site as a whole.



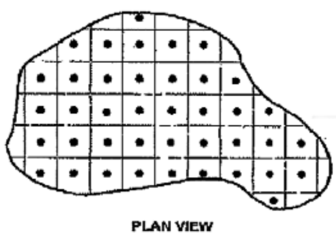


Systematic grid sampling is a statistically based sampling strategy. Sample locations are selected at regular intervals throughout the site area on a grid pattern, with the first sampling location chosen at random to lessen bias.

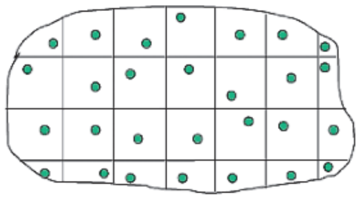
Situations appropriate to the use of systematic sampling include:

- site validation of both residual soil and backfill material
- to detect hotspots
- estimating the mean concentrations of contaminants
- general site characterisation in the absence of adequate site history information

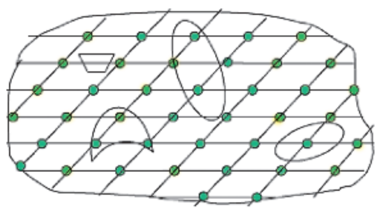
Systematic grid sampling involves subdividing the area of concern by using a square, triangular or herring-bone grid and collecting samples from the nodes (intersections of the grid lines).



Systematic random sampling is a useful and flexible design for estimating the average pollutant concentration within grid cells, and is sometimes also referred to as stratified random sampling

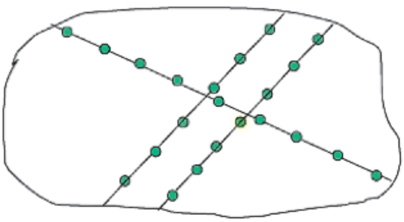


Search sampling utilizes either a systematic grid or systematic random sampling approach to search for hot spot areas. The smaller and/or narrower the hot spots are, the smaller the grid spacing must be in order to locate them. Also, the smaller the acceptable error of missing hot spots is, the smaller the grid spacing must be. This, in effect, means collecting more samples.



Hot spots are marked with different shapes

Transect sampling involves establishing one or more transect lines across the surface of a site. Samples are collected at regular intervals along the transect lines at the surface and/or at one or more given depths. The length of the transect line and the number of samples to be collected determine the spacing between sampling points along the transect. Multiple transect lines may be parallel or nonparallel to one another.



In practice, an investigation of a site for the presence of hazardous substances normally involves the use of more than one sampling pattern. If a predetermined sampling point needs to be relocated (eg, due to a physical obstruction), then the deviation from the sampling pattern should be documented.

Selection of sampling points

Sampling points may be located with a variety of methods. A relatively simple method for locating random points consists of using either a compass and a measuring tape, or a pacing, to locate sampling points with respect to a permanent landmark, such as a survey marker. Then plot sampling coordinates on a map and mark the actual sampling points for future reference.

Sampling equipment

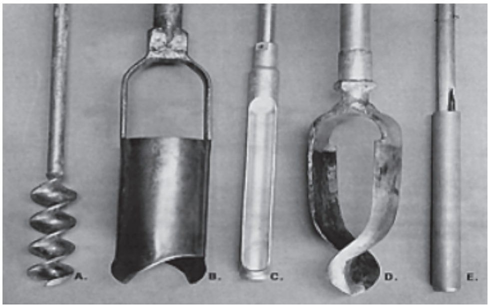
The following techniques can be considered when undertaking soil sampling:

◆ **surface and shallow subsurface grab sampling**

Soil samples can be collected using an appropriate hand trowel, push tube, plastic scoop or shovel. This is a quick and efficient method to collect shallow surface and subsurface samples.

◆ **hand auger sampling**

A hand auger is a sampling device manually or mechanically driven into the soil, with typical dimensions excavated of between 6 cm and 15 cm in diameter. Sampling depths up to 2-3 m can be easily achieved, depending on soil type, and greater depths are sometimes possible.



◆ **test pit sampling**

Test pits are excavated using a backhoe excavator, but may also be hand dug. Typical dimensions are rectangular pits of around 3 m length, 1 m breadth and 3-4 m depth. Test pits enable visual inspection of the shallow strata and can be extended into trenches to observe the extent of strata or visible contamination.

The mechanical method by which a sampling tool collects the sample may impact representativeness. For example, if the sampling objective is to determine the concentrations of contaminants at each soil horizon interface, using a hand auger would be inappropriate: the augering technique would disrupt and mix soil horizons, making the precise horizon interface difficult to determine.

B. Steps during the visit

Physical characterization and climatic conditions

All possible data concerning the physical characterization of soil including its type and the climatic conditions of the sites are recorded with the help of simple tests (e.g. soil coulor, grain size, compaction – penetration test)

Sample collection

In general, you should keep in mind that the larger the number of samples collected from a site and the larger the volume of each sample, the more representative the analytical results can be.

● Sample number: The number of samples needed vary according to the particular sampling approach that is being used, the level of confidence required for the investigation, the area of the site, site-specific constraints/limitations, and budget. For example, in grid sampling, one sample is generally collected at each grid node, regardless of grid size, and once contaminated grid node samples are located, adjoining grid cells can be sampled more thoroughly to define areas of contamination. The number of samples may be weighted towards near-surface sampling for assessing health and ecological risks from exposure to soil contaminants. If groundwater is considered to be a potential pathway or receptor, then an increased number of samples collected from near the water table may be selected for analysis.

● Sample volume: Soil samples should be collected at two or more depths to establish the vertical extent of contamination. The sample depth and the soil profile (eg, fill material, topsoil, humus/ leaf litter) from which the sample was collected must be recorded and considered as part of the data interpretation. Soil samples can be collected from throughout the soil profile, from the surface (0-15 cm), at regular intervals (every 25-100 cm), at any change in strata, and at the depth at which contamination is anticipated or observed. Samples should generally not be collected from across different strata (for example across the boundary between natural ground and fill). Surface samples are defined as no deeper than 15 cm, and are typically collected from 0-7.5 cm. For surface samples, collect soil over a surface area of one square meter per sample. A square cardboard template measuring 30x30 cm, or a round template with a 10 cm diameter can be used to mark sampling points.The collection of surface soil samples deeper than 15 cm increases the possibility of dilution of the surface soil sample by mixing with less contaminated subsurface soils.

● Composite sampling: Composite sampling consists of collecting individual samples from different locations and bulking and mixing an equal mass of the samples (called sub-samples) together to form one composite sample. A composite sample can then be analysed, and represents the average of the constituent sub-samples. The use of composite sampling should only be undertaken by experienced site investigators after full consideration of the site history. Compositing can be used to determine an acceptable disposal location, or for characterising sites with similar contaminant levels (such as horticultural sites).

Background samples

Background samples are collected in the area near the site that is not affected by the contaminant sources on the site. Background samples determine the natural composition of the soil and are considered “clean” samples.

Background samples provide a basis for comparison of contaminant concentration levels with naturally occurring levels of target analytes in the soil samples collected on site.

Background samples can help to show whether contaminants present on a site are due to wider area effects, either natural or artificial. Suitable locations for background samples should be chosen based on the:

- site geology (background concentrations of metals are related to the parent rock types)
- site history (should indicate no disturbance at the location)
- topography (sample collection should not be from any low-lying areas, such as ditches, but from areas of raised ground).

Sample locations and labels

Once a soil sample is collected it should be clearly and uniquely labelled. Records kept for should include: a unique sample reference number, date, time, depth and location collected, sampler's name, any site observations and weather conditions.

Sample handling

Sample containers should be supplied by the analytical laboratory and must be clean and of an appropriate size for the analyses to be undertaken. The sample containers should be handled so as to ensure the integrity of the sample is not compromised during storage. Keep samples in sealed containers away from sources of heat and protected from light, and deliver to the laboratory for analysis.

Decontamination

Decontamination procedures include the process of washing, rinsing and removing material from exposed surfaces of equipment and clothing that can, or has, come into contact with the sample. Any decontamination must be undertaken in a manner that avoids contaminating areas to be sampled, or the spread of contamination around or off the site.

ANNEX 4
EXAMPLES FOR THE USE OF PROSODOL MONITORING TOOL

The Monitoring Application Tool developed during the PROSODOL project is user friendly and can be used by the owners of OMWs disposal areas to monitor the quality of soil of their land just by inserting the results of the chemical laboratory of some predefined soil parameters.

The software permits the monitoring of:

Organic Matter, %
Electrical Conductivity, mS/cm
Total Nitrogen, %
Total Polyphenols, mg/kg
Available Phosphorous, mg/kg
Exchangable Potassium, cmol/kg
Available Iron, mg/kg
pH
Total Nickel, mg/kg**
Total Chromium, mg/kg **
Total Molybdenioum, mg/kg**

The parameters with bold characters should only be monitored in case that mills' steel equipment is composed by an alloy of inferior quality than 316 (mainly old mills)

For an efficient monitoring, you should follow the steps:

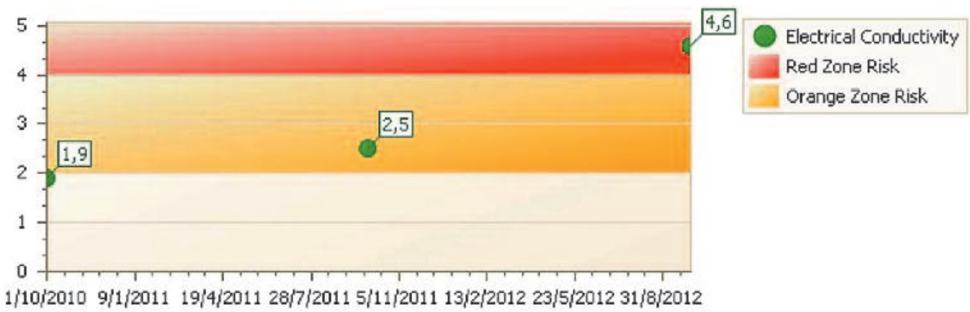
1. A sampling strategy should be designed, preferable with the assistance of an expert (e.g. agronomist).
2. Collect soil samples according to the guidelines of Annex 3 and of your agronomist.
3. Send the samples as soon as possible to the chemical laboratory
4. Insert the results of the analysis to the specific page of the monitoring tool (see the respective manual).
5. Be very careful with **number units!!!** The units of the inserted measurements should be the same as in the respective page of the software and also as mentioned above.
6. When measurements have been inserted, the graphical representation of the parameters relative to sampling period will appear.
7. Points in the white area are considered normal.
8. Points in the orange area are considered very high and measures should be taken. For this you should ask for an expert's advice and assistance.
9. Points in the red area are considered excessive and risky and immediate measures should be taken. Stop any type of activity relative to the addition of OMWs on soil immediately (irrigation, disposal) and ask for advice and assistance by experts.

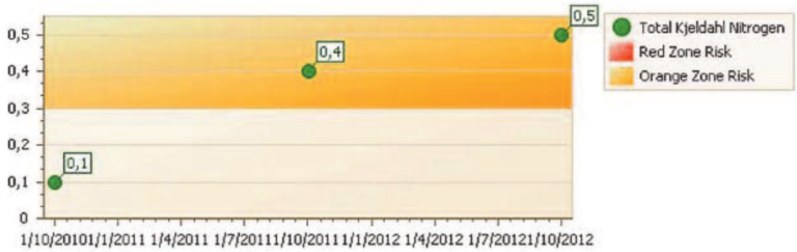
AN EXAMPLE

The following Table includes indicative values for the eight soil paramaters as measured for a disposal area in 2010, 2011 and 2012.

These are the graphical representations of the Soil Indicators. From the graphs you can easily identify any negative effect on your land quality characteristics and take the appropriate measures.

Soil Indicator	2010	2011	2012
Organic matter, %	3.5	4.5	3.6
Electrical Conductivity, mS/cm	1.9	2.5	4.6
Total Nitrogen, %	0.1	0.4	0.5
Total Phenols, mg/kg	35	90	178
Exchangeable Potassium (K), cmol/kg	1,8	2.1	3.9
Available Phosphorous (P), mg/kg	25	65	134
Available Iron (DTPA-Fe), mg/kg	35	87	125
pH	7.6	7.7	7.5




0,5
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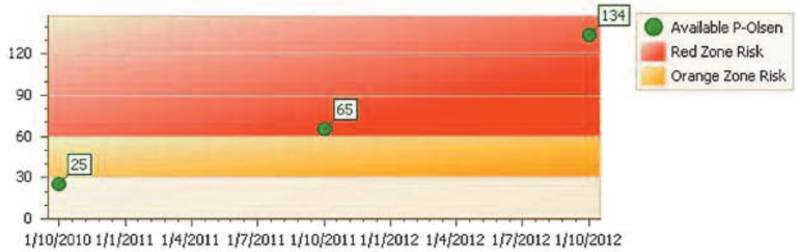
Total Kjeldahl Nitrogen
Red Zone Risk
Orange Zone Risk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Available P-Olsen
Red Zone Risk
Orange Zone Risk


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Exchangeable K
Red Zone Risk
Orange Zone Risk


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125
1/10/2010
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1/7/2011
1/10/2011
1/1/2012
1/4/2012
1/7/2012
1/10/2012
Available (DTPA)-Fe
Red Zone Risk
Orange Zone Risk

Further reading

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Το έργο
LIFE-PROSODOL
χρηματοδοτείται
κατά 50% από την
Ευρωπαϊκή Ένωση