HELLENIC REPUBLIC

NATIONAL AND KAPODISTRIAN
UNIVERSITY OF ATHENS,
DEPARTMENT OF CHEMISTRY, SECTION III,
INORGANIC, ENVIRONMETAL CHEMISTRY
AND TECHNOLOGY

Green innovative biodegradation of polyphenols in oil mill wastewaters to produce first class soil conditioner

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Olive oil production worldwide

- Olive oil is a key ingredient of the Mediterranean diet and its consumption is rapidly increasing worldwide.
- <u>According to the International Olive Oil Council:</u>

Olive oil production : **70%** since 1987

2,861,500 tons for the 2009/2010 period

75% comes from Mediterranean Region

<u>Serious environmental problems :</u>

High amounts of by-products

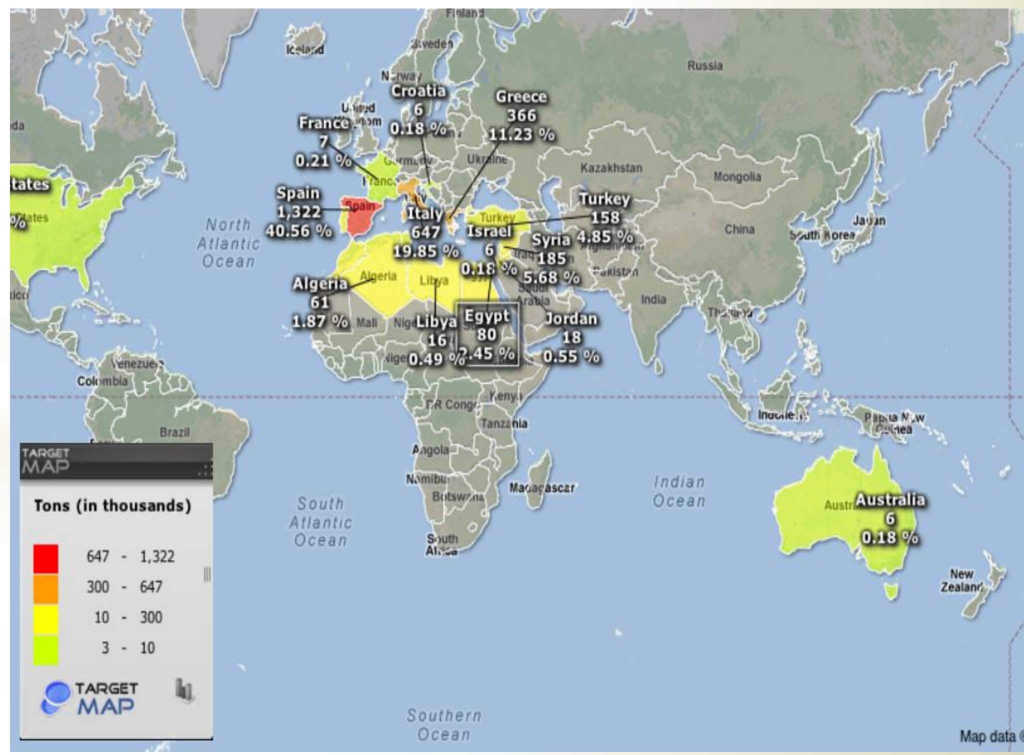
3 – phase systems

- olive pomace (OP)
- olive mill wastewater (OMWW)

2 – phase systems

- two-phase olive mill waste (TPOMW)

✓Total amount of OMW~ 10 million m^3/year



Characteristics and composition of Olive Mill Waste Water from 3 - phase OM

Main characteristics of OMWW:

- high chemical oxygen demand (COD) concentration (45–220 mg/L)
- low pH (4–5),
- high suspended solids concentration (up to 50 g/L)
- other recalcitrant organic compounds, water-soluble phenols and polyphenols originating from the olives

Typical OMWW composition by weight:

- 83–94% water,
- 4–16% organic compounds
  - sugars, polyphenols, polyalcohols, pectins, and lipids, nitrogenous compounds, organic acids, carotenoids, tannins
- 0.4–2.5% mineral salts
  - chlorides, sulphates and phosphates, potassium, calcium, iron, magnesium, sodium, copper.

Environmental degradation from OMWW

Usual treatment and disposal practice followed in Greece – environmental impacts:

- Neutralization with lime and disposal in evaporation ponds/lagoons.

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- ➢ overflow and affect neighbouring systems
- ➢ Polyphenols and other organic compounds → high COD → low Dissolved Oxygen → induction of anaerobic conditions → odor nuisance

- Direct disposal into soil, sea or rivers.

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- ➢ Oil compounds → increased soil hydrophobicity and decrease water retention and infiltration rate
- ➢ Polyphenols → bactericide and phytotoxic properties cause alterations in N cycle, changes in soil microbial activity as well as contamination of surface- and groundwater.
- ➢ High phosphorus contents → eutrophication
- ➢ Lipids form an impenetrable film, blocks out sunlight and oxygen → hypoxia

Bioremediation through composting of OMW

Advantages			Disadvantages		
Reduction of organic pollutants	Integrated olive oil mill wastes management	End-product is a neutralised compost material	Time consuming process (8-12 months)	Need for large land area	Product is often not the expected due to dependence on many parameters.

Compost

- organic matter source
- increases soil fertility and the cation exchange capacity
- improves soil water capacity
- favors microbial activity in the soil
  - helps in the breakdown of pesticides and other organic substances
- acting sedative in the development of soil-borne pathogens
- reduces the bioavailability of heavy metals

Biocatalytic micro - aerobic treatment of OMW

Materials

- Olive mill waste waters from 3-phase mill
  They may be replaced by 2-phase mill wastes
- All plant materials that remains in olive mills before olive oil extraction. They may be replaced by other green residues.
- Biocatalyst

Method:

- Mixture of OMWW and crushed plant residues, 50:50
- Addition of biocatalyst
- Stacking of the composting mixture to piles
- Monitoring of physicochemical parameters
- Aeration of the mixture
- Wetting whenever moisture < 50%
- Biostabilization for 2 months

Biocatalyst ☆

Innovative solid substrate based on a special organic rock, mineral origin, inoculated with soil microorganisms laboratory cultivated.

☆ Patent 2004010018 (2004) Owner Dr Dinos Chassapis Ass. Professor University of Athens

Typical analysis:

- Microorganism population (Bacteria, mycetes, actinomycetes,) 2. 10^9 c.f.u./g
- Humic substances 30% (dry basis)
- Mineral content 38% (dry basis)

* Accelerates 5 times the biochemical reactions in the compost.
* Enhance the bio-oxidative phase of composting

necessary microorganisms for the decomposition of polyphenols, carbohydrates, lipids and other organic substances

Humic acids

* Operating at wide ranges of pH
* Suitable for Mediterranean climate conditions.
* Active even in extreme environments

Physicochemical parameters

Parameter	OMWW	Initial mixture	Soil conditioner (60 days)
Moisture (%)	90.3	68.1	48.9
Electrical conductivity (mS/cm)	41	1.92	1.8
pH	5.48	5.7	7.3
Bulk density (g/ml)	0.98	0.33	0.4

Electrical conductivity for initial mixture and soil conditioner has measured in ratio 1:5 in water and pH in 1:10.

Chemical analysis – maturity indices

Changes in some critical parameters during composting (dry weight basis)

Parameter	OMWW	Initial mixture	Soil conditioner (60 days)
Ash (% w/w)	7.3	14.0	21.9
Organic matter (% w/w)	92.7	86.0	78.1
Total organic carbon (% w/w)	53.8	49.9	45.3
Total Kjeldahl nitrogen (% w/w)	1.7	1.3	1.3
C/N	31.6	38.4	34.8
Humic acids (% w/w)	n.d	5.8	8.0
Total phenols mg/kg	374.3	80.3	32.3

10%

91.4% reduction of polyphenols

Evaluation of OMW soil conditioner as Soil Media

Parameter	Mean value of produced Soil Conditioner	Soil Substrates /media (Optimum values)	Soil Substrates of sowing /nurseries (Optimum values)
Total organic content (TOC) % w/w	78,1	-	80,0[a]
pH	7,3	5 – 7,5	5,5-7
Electrical conductivity (EC) (dS m^{-1})	1,8	≤3.5 [a]	≤0,5[a]
Total N % w/w	1.3		
Cu (mg kg^{-1})	40		<500 [b]
Zn (mg kg^{-1})	123		<1500 [b]
Cd (μg kg^{-1})	0,20		<5 [b]
Cr (μg kg^{-1})	0,10		<200 [b]
Ni (μg kg^{-1})	28		<100 [b]
Pb (mg kg^{-1})	0,05		<1000 [b]

Physical parameters evaluation OMW compost

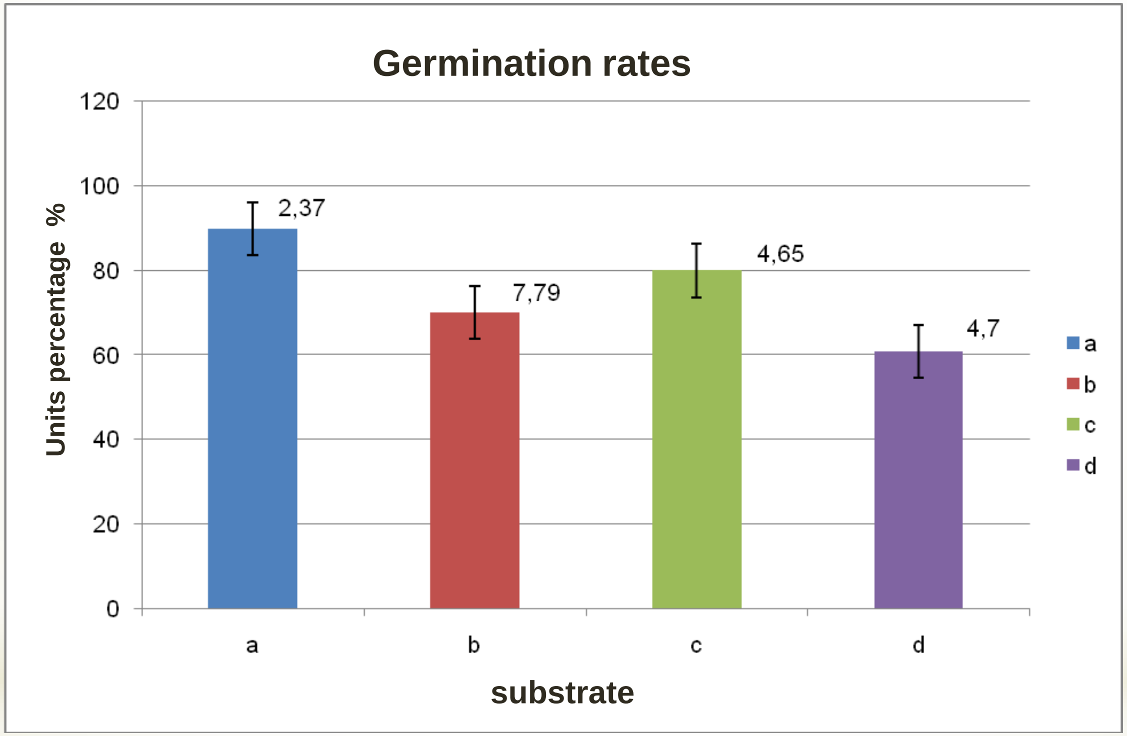
Soil Medium for growing plants	Produced OMW soil conditioner	Optimum Soil Substrate
EAW (vol %) + WBC (vol%)	49,8-60,0	55-65
AS (vol%)	15,6-30,8	20–30
TPS (vol%)	73,5-80, 7	85
Bulk density g. L^{-1}	440-500	400

EAW: easily available water, AS: air space, WBC: water buffering capacity and TPS: total pore space

Comparison of composts produced from OMWW in Greece

Parameter	Produced Soil Conditioner	Compost from OMW Greek -1st	Compost from OMW Greek-2nd
water buffering capacity (%)	147.8	248,7	n.a.
Humic Acids (%)	8	5,84	n.a.
Electrical conductivity (dS / m)	**1,7**	**2,2**	**1,1**
pH	7.3	7,7	7,5
Organic Matter (%)	78.1	74,1	39
Microrganisms (c.f.u. / g)	**23 .10^{8}**	**3,6 .10^{8}**	**n.a.**
N %	**1.3**	**1,0**	**1,4**
P (ppm)	n.a.	445	48,7
K (%)	n.a.	0,7	0,32
Zn (ppm)	123	49.7	20.1
Cu (ppm)	**40**	26.7	6.9
Ni (ppm)	28	n.a.	n.a.
Cd (ppm)	0,18	n.a.	n.a.
Pb (ppm)	0,05	n.a.	n.a.
Cr (ppm)	0,1	n.a.	n.a.
Hg	**Ø**	n.a.	n.a.
Escherichia coli, Salmonella Spp. (Enterobacteriaceae)	**Ø**	n.a.	n.a.

Preliminary experiments on lettuce, Lactuca sativa (Asteraceae) based on three parameters *



I. Germination rates

Used as a growth substrate 4 mixtures

a- 100 % v/v Perlite

b- 50 % v/v Perlite : 50 % v/v OMW produced soil conditioner

c- 66.66 % v/v Perlite : 33.33% v/v OMW produced soil conditioner

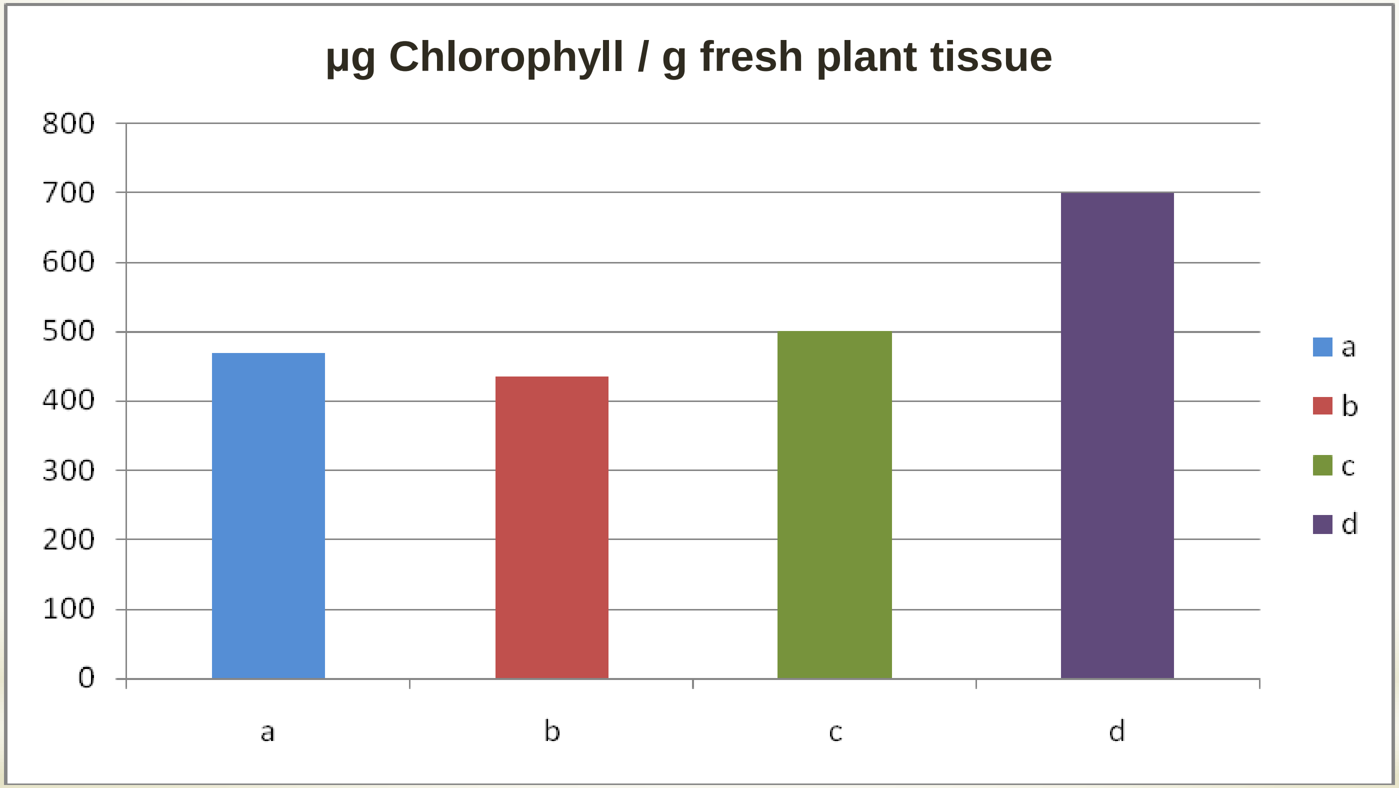
d- 100 % v/v OMW produced soil conditioner

***University of Athens Department of Biology, Plant Ecophysiology Laboratory**

II. μg Chlorophyll / g fresh plant tissue

Preliminary experiments on lettuce, Lactuca sativa (Asteraceae) seedlings growth under the influence of the produced OMW soil conditioner, based on weight of Chlorophyll / plant tissue

Used as development substrate 4 mixtures



a- 100 % v/v Perlite

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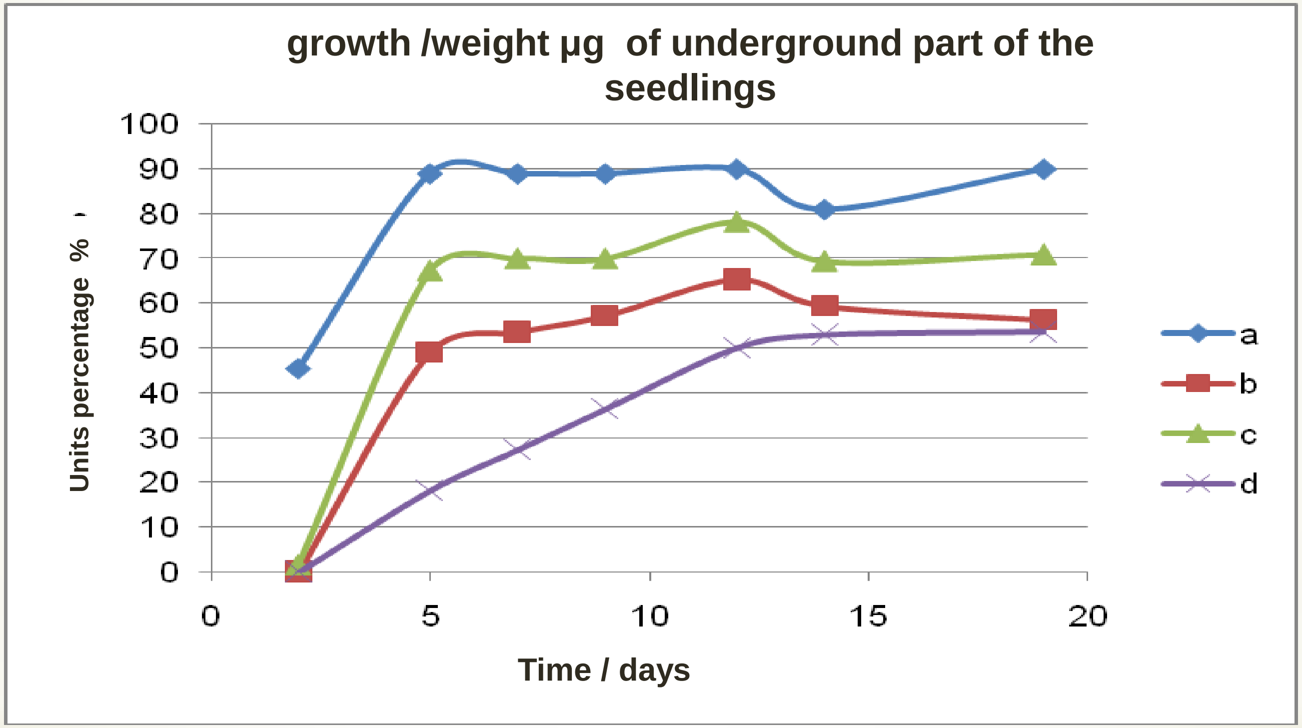
III. Growth of the underground part of the plants



a- 100 % v/v Perlite

b- 50 % v/v Perlite : 50 % v/v OMW produced soil conditioner

c- 66.66 % v/v Perlite : 33.33% v/v OMW produced soil conditioner

d- 100 % v/v OMW produced soil conditioner

Preliminary experiments* on VEGETABLES and ORNAMENTALS growth under the influence of the produced OMW soil conditioner

FIELD EXPERIMENTS ON VEGETABLES

During the planting seedlings on the line:
50 plants by adding 250g «produced soil conditioner" in the planting pit,
50 plants by adding 250g other compost from OMWW in planting pit
50 plants by adding 500g «produced soil conditioner"
50 plants by adding 500g other compost from OMWW in planting pit;
50 plants without any soil conditioner (control)

POT EXPERIMENTS ON ORNAMENTALS

Usage in containers filling with roses, geranium, bougainvillea, jasmine as a supportive medium with red soil about 30%, in flower beds of herbaceous sensitive floriculture, palm trees, Benjamin, etc. to improve soil structure.
The above was used instead of classical peat

- Showed no phytotoxicity as soil medium component in vegetable plantations and ornamental plants.

- Logged positive effect on plant growth

- Could replaces common used soil substrates much more expensive

***Experiments performed in the farms of the Union of Agricultural Cooperatives of Rethymnon, Crete**

Conclusions

- Proposed method is low cost of investment and operation, converts a toxic waste into a soil conditioner product
- Reduced production time (2 months compared to 12 and 18 months common procedure).
- Chania soil conditioner shows positive effect on plant growth and
- Can replace the more expensive black-humus peat.