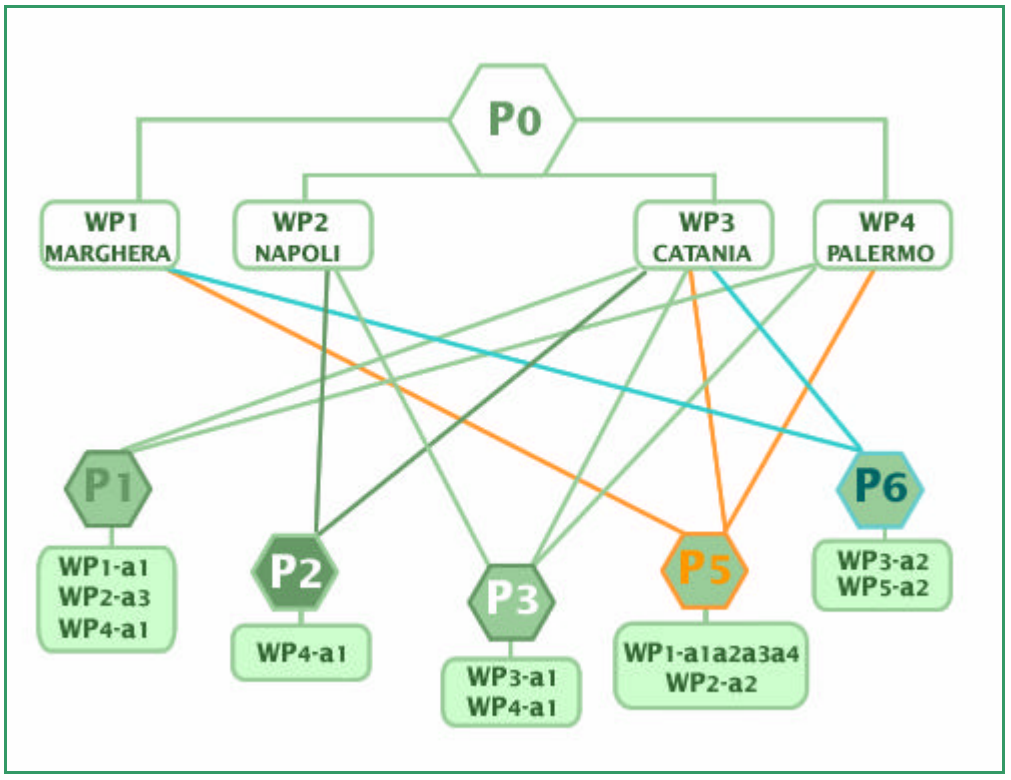
Interuniveristy National Consortium
"Chemistry for Environment"

LAW 488/92 Cluster 11 "Land Environment"
THE SIX PROJECTS MANAGED BY INCA
(P0, P1, P2, P3, P5, AND P6)
Brief description updated to year 2000



P0 – GENERAL PLAN FOR STRENGTHENING THE FACILITIES OF THE CONSORTIUM: ESTABLISHMENT OF TWO NEW LABORATORIES IN NAPOLI AND PALERMO, ENHANCEMENT OF THE EXISTING LABORATORIES IN MARHERA-VENEZIA AND CATANIA.

The Interuniversity National Consortium "Chemistry for Environment" has 27 member universities all over Italy. Despite of this network, up to present days, the Consortium fully owns and manages just one laboratory. It is hosted at the facilities of the VEGA "VEnice GAteway", the scientific and technological park of Venezia (Venice), located on mainland in Marghera.

The long-term politics of the Consortium provides the establishment or strengthening of some nodal units according to the distribution of the member universities nationwide. The project is subdivided into four workpackages (WP1-WP4) corresponding to the nodes of Marghera (WP1), Napoli (WP2), Catania (WP3), and Palermo (WP4).

Besides the analytical facilities of Marghera, the Consortium wants to acquire new laboratories or upgrade equipment at some nodes all over Italy. Accordingly, the purchase of an high resolution Inductively Coupled Plasma Mass Spectrometer (ICP-MS) in Catania was already

decided. This instrument represent the first high valuable equipment, fully owned by the Consortium, in an area of the Objective 1 (heavy depressed areas of Italy). For a valid interaction between the Chemical Sciences Department of the University of Catania and the INCA network, the Consortium signed an agreement with that University. Further nodes with analytical facilities will be created at the member Universities of Napoli and Palermo.

In a first phase, these three laboratories should partially satisfy the needs of the headquarters located in the Southern and Central-Southern areas of the Consortium network.
The present project provides the strengthening of the node of Marghera, both in terms of premises and equipment. It also includes the upgrade and increase of instrumentations of the Consortium located in the node of Catania. Finally the project has provisions for acquirement of self-owned equipment by the Consortium at the headquarters of Napoli and Palermo.

P1 – RECYCLING OF BIOMASSES, AGRICULTURE WASTES AND POLYMERIC MATERIALS THROUGH PYROLYSIS AND PRODUCTION OF ACTIVATED CARBONS.

European regulations for environment protection privileges the recycling of non-toxic solid wastes, with respect to discharge in landfills or incineration.

In the project a thermal process is used to get activated carbons form solid wastes, followed by their activation. Those "carbons" will be tested for adsorption of liquid and gaseous pollutants and for environmental catalysis (abatement of gaseous contaminants and low-impact reactions).

This project focuses on research at a pre-competitive level. Being interconnected to the other INCA projects for Law 488, it will take advantage of the facilities of the INCA network. The project is subdivided into four workpackages, and respective sub-workpackages.

WP1 – Characterization and analysis of biomasses, agriculture wastes, and polymeric materials.

The characterization of wastes of an organic and polymeric nature, to be used as feedstock for pyrolysis processes, is important to guarantee quality of the final product. This is a preliminary phase for all the P1 project. The chemical composition of some proper solid wastes (produced in South of Italy) will be analysed in order to assess energy required for pyrolysis and economic value of the final product.

WP2 – Pyrolysis of wastes and polymeric residues, biomasses and agriculture leftovers.

The pyrolysis of wastes for their recycling as activated carbons will be studied on a laboratory scale. During this phases we plan to obtain a carbon-rich material which can be subsequently activated. Two plants will be realised one for polymeric materials and one for organic wastes in order to optimize yield of the process and price/quality ratio of products.

WP3 – Abatement of pollutants with functionalised activated carbons.

Activated carbons will be functionalised and tested for adsorption processes in solid-liquid and solid-gas phases. The quality of these "carbons" depends on nature and quantity of the functional groups. These factors will be optimized in order to get maximum efficiency, also using computer modelling for interpretation of results and transfer of the process at an industrial scale.

WP4 – Activated carbons adsorbed with metals and environmental catalysis.

Activated carbons will be tested as supports for metals and tested as catalysts for the abatement of NO_x and for carbonylation and reduction reactions. These factors will be optimized in order to get maximum efficiency, also using computer modelling for interpretation of results and transfer to an industrial scale.

P2 – RECOVER AND ECO-COMPATIBLE DISPOSAL OF WASTEWATERS WITH HIGH PHENOL CONTENT FROM FOOD INDUSTRY, USING CHEMICAL AND BIOLOGICAL PROCESSES.

Common biological water depuration plants often do not fit for purification of wastes from food industry due to the presence of biocide and recalcitrant molecules. Specific studies are needed to find out if a chemical (pre-) treatment is applicable as standalone method or for integration of biological processes. The final goal is that of designing proper depuration plants. In Italy oil mill wastewaters (the so-called "vegetation waters" from olive oil production) have a major environmental impact because of high production (3×10^{10} litres per year) and presence of phenol compounds.

The present regulation (Law 574/96) allows controlled disposal of vegetation waters on cultivated soils, even if definitive indications about their polluting potential are lacking, especially in relation to underground water layers.

The purpose of this project is to find out a biological solution to the problem, also creating a pool of experts for environment protection in the sector of olive oil production which is an important activity of food industry in many zones of Objective 1.

A network involving university, research centres, and private companies is an added value with an elevate potential, allowing the design of integrated interdisciplinary methods. The final goal is to shift from an "end of pipe" approach to a "prevention" one.

WP1 – Development of chemical and biological protocols for disposal and valorisation of phenol compounds in vegetation waters from oil mills.

The objective of the WP is to find treatments for vegetation waters to degrade the most toxic and recalcitrant phenolic components. This both detoxifying those or bio-converting them in reusable products. The idea is a combined process using light and algae. In a first phase all pollutants will be isolated and identified. In a second phase phenol-resistant strains of algae will be isolated and their degrading capabilities will be investigated. Also heterotrophic bacteria can be used to this purpose. Phenotypic and genetic features will be studied as well. In a last phase we will investigate which products are yielded from the photochemical treatment of phenolic compounds and their mixes.

WP2 – Electrochemical and biological combined treatment for degradation of toxic and/or recalcitrant compounds.

The objective is to find a profitable plant with simple realisation and management to operate a pre-treatment of the wastewaters. This should lower toxicity and organic load of the liquid wastes, so that they can be disposed to a common activated-sludge plant. The electrochemical treatment is not designed for a complete mineralization but for oxidation of the refractory part of the molecule and to make this biodegradable and to abate toxicity of the molecules to a level compatible with survival and degradation activities of the micro-organisms.

W3 – Anaerobic treatment of wastes from food industry.

Biodegradability and molecular structure of phenols have not been definitively correlated yet, nor involved enzymes have been described. In the project the capability of adaptation of the strain *Thauera aromatica* to non-phenolic aromatic substrates will be investigated. Induced substrate-specific enzymes will be isolated and characterized.

An alternative to degradation to non-toxic compounds of phenols may be the bioconversion to reusable products. A possible pathway will be studied in this project: the *in vitro* conversion of phenol to 4-hydroxybenzoic acid using the enzymatic pool of *Thauera aromatica*.

WP4 – Development of methods for chemical and biological treatment of wastewaters from food industry.

Since direct biodegradation of vegetation waters from oil mills is hard to obtain, a pre-treatment is advisable. One method involves use of oxidants immobilised on proper solid supports. Both oxidants and supports will be investigated in this project, in order to get a better transformation of substrates.

The biological treatment will then eliminate or reduce the organic load and give indications about the validity of the chemical pre-treatments. The latter will be modulated using results of toxicological tests performed in different phases of the treatment.

P3 – REMOVAL OF POLLUTANTS USING PHOTOCATALYTIC AND MEMBRANE PROCESSES.

Both photocatalytic and membrane processes show innovative aspects which are favoured by present European regulation for environment protection. Moreover the two techniques may be combined.

Different research groups will be coordinated in this project in order to line up a pool of young and advanced experts and design the new technology. Moreover the technique will be designed considering future real applications on larger scale.

WP1 - Abatement of pollutants through heterogeneous photocatalysis on membranes.

Selection and preparation of best crystalline semiconductors to be used for realisation of photocatalytic membrane reactors in aqueous liquid phase. Selection of best techniques for preparation of photocatalytic membranes containing immobilized crystalline semiconductors. Design and realization of photoreactors using the membranes at a laboratory scale and determination of their performance in aqueous phase. Computer modelling of the studied photoreactors.

WP2 - Depuration of wastewaters from food industry using photocatalytic processes.

Design, realization, and modelling of heterogeneous photoreactors optimized for treatment of wastewaters from food industries. Selection of the best photoreactor according to the matrix to be treated from a technical, operative, and economic point of view. Certified models of reactors will then be used for depicting scaling-up scenarios and *on-field* application.

WP3 - Study of selective carriers on membrane support for removal of metals from waters.

The aim is to gather quantitative information on membranes with carriers for removal of metals and other toxic non-biodegradable contaminants from liquid aqueous wastes from food industry. The basic idea is to use new macrocyclic ligands, essentially based on the calixarene. Once ligands are identified and properly purified, the characteristics of the formation of the pollutant-ligand complex will be studied in order to get optimal selectivity (e.g. linking $^{137}Cs^{+}$, $^{90}Sr^{2+}$, and/or Pb^{2+}, but not Na^{+} or K^{+}).

Afterwards, the objective is to realize expert systems able to identify and select the species of interest. Facilitated transport systems based on PIM for removal at a bench scale of metallic cations. Removal will also be performed using ionic cromatography with calixarenes covalently linked to silica gel. Furthermore the coupling of sequestration ability of those macrocycles and sensitivity of piezoelectric sensors (QCM) will be exploited for identification and quantisation of metallic cations.

WP4 - Direct and sensitized photodegradation of contaminants in wastewaters.

The long-term goal is to identify a proper photochemical and/or photooxidative technology for organic pollutants (especially plant protection products), in order to transform them in non-toxic or

readily-degradable compounds. For this purpose it is necessary to check photodegradation extent and bio-mimetic conditions at a lab scale, then verify toxicity of the treated solutions.

P5 – METHODS FOR SYNTHESIS WITH LOW ENVIRONMENTAL IMPACT.

Nowadays environment protection is a concern of all industrial countries. A relatively new approach to tackle the problem is that of Green/Sustainable Chemistry (GC) . This discipline radically changes the point of view in environment protection, shifting the solution from the "end of pipe" to the beginning of the process, so preventing pollution.

Research in GC is versatile and interdisciplinary. A GC traditional approach is that of selective synthesis which produces few by-products and the design of safe reaction conditions, which also minimize emission of solvents in the atmosphere. A new GC area is that of the use of natural renewable resources which, thanks to biotechnology, yield chemical intermediates with high added value. For this purpose a general goal of this project is the education of some young experts in the area of GC.

Future issues in GC for safer reaction conditions and environment protection regard substitution of dangerous catalysts, wide use of immobilised catalysts, reactions with immobilised reagents and catalysts. Some specific actions are necessary like substitution of intermediates containing chlorine (e.g. dimethylcarbonate may substitute fosgene in solid foams production). Another need is valorisation of natural resources coupled with use of biotechnology to produce valuable intermediates of reaction or for production of biodegradable "plastics", dies, etc. Another example is substitution of volatile organic solvents with safer products (e.g. use of supercritical carbon dioxide).

WP1 – Use of eco-compatible solvents and reagents.

The objective is the design of new syntheses to be used in chemical or pharmaceutical industry, using low environmental impact solvents and reagents. Studies about the use of derivatives of lactose for production of biologically active disaccharides or oligosaccharides for exploitation of renewable resources.

The project provides investigations about optimisation of reaction conditions in order to increase: selectivity (while abating by-products), safety of reaction conditions, and economic feasibility. This through:

1) design of plug-flow technology for studies of reactivity of dimethylcarbonate as methylating and metoxycarbonylating agent;
2) use of zeolites as catalysts in systems optimized for adsorption of reagents/products or to support metal catalysts for synthesis of dimethylcarbonate from carbon dioxide and methanol;
3) catalytic systems using transition metals active in bland conditions for reactions of carbonylation or hydrogenation;
4) solid catalytic systems with high acidity and efficiency for substitution of acids and superacids in liquid phase syntheses;
5) low environmental impact reactions for production of chiral "building blocks" for syntheses of drugs containing pure enantiomers (antitumorals, cell signalling, etc.).

WP2 – Use of carbon dioxide and organic carbonates for low environmental impact syntheses.

The long-term goal of this workpackage is to conceive methods for new carboxylation syntheses using carbon dioxide and organic carbonates. CO_2 will be used as building block of organic molecules using photocatalysis, while carbonates will be used for carbamating reactions. This through:

1) Preparation and characterization of semiconductors with photocatalytic activity for reduction of CO_2. Functionalization of organic molecules with insertion of CO_2 using proper combinations of semiconductor and substrate. Study of reaction mechanisms and kinetics.
2) Design and setup of new synthetic pathways for methyl-N-aryl-carbamates via aminolysis of methylphenilcarbonate (a substitute of phosgene) by aromatic amines. Study of proper catalytic systems for carbamating reaction with high yield and selectivity.

P6 – IN-SITU AND EX-SITU TECHNIQUES FOR REMEDIATION OF CONTAMINATED SOILS.

The project aims to study at a laboratory scale, or - in proper circumstances - at a larger scale, techniques for soil remediation, in order to identify the proper method for specific real cases. Techniques will have biological, chemical, and physical (thermal treatment, immobilization of metals) nature.

New methods for analysis of trace (or low concentration) pollutants will be investigated with special reference to halogenated biphenyls, halogenated diphenylethers, dibenzofurans, halogenated dioxins, and polycyclic aromatic hydrocarbons (PAHs). A database with the best techniques for different combinations of contaminants and type of soil will be created. The database will be available for public consultation (public agencies, etc.).

The extension of the INCA network will make it possible to collaborate with local ruling bodies and private agencies in a multidisciplinary framework and to train a pool of young experts in the field of soil remediation all over Italy.

WP1 - Creation of a database for remediation techniques. Application of chemical and combined methods and thermal treatments for soil recovery.

Three specific actions are part of this workpackage:
a) Creation of a database containing toxicological data about soils and available remediation techniques according to characteristics of soil/pollutant. Case-studies will be included as well as literature references. The risk analysis (WP5) will complete the database.
b) Investigations for chemical soil remediation, also via extraction of pollutants with supercritical fluids.
c) Thermal treatments for abatement of organic pollutants in soils.

WP2 – Tests for chemical metal-assisted oxidation techniques for organic pollutants, using oxygen or peroxides as oxidative agents.

This workpackage is dedicated to the study of potential of abiotic reactions for decontamination of soils. Oxidation reactions and their correlation with the molecular structure of widespread and/or recalcitrant pollutants. This considering that, sometimes, soil may be a “difficult” matrix for microbes to live and carry on their detoxifying processes. In these cases, the project wants to identify the best combination of biotic/abiotic processes which may make the remediation possible.

WP3 – Optimisation of pollutant extraction in supercritical phase.

This workpackage wants to explore potential of extraction of pollutants using supercritical solvents for remediation of soils. An ambitious goal is that of coupling extraction and degradation of contaminants. In order to achieve these results, proper design of extraction methods and quantitative analysis of pollutants will be performed (i.e. using Gas Chromatography/Mass Spectrometry combined with infrared spectroscopy). Modelling derived from another running project may be used to find mathematical models to classify samples of polluted soils.

WP4 – Techniques for immobilization and removal of metals from soils.

The mining activity for extraction of polymetallic sulphides generated millions of tons of toxic wastes containing lead, zinc, copper, cadmium, arsenic, and/or mercury. Public funds for recovery of such areas are often attainable, but economically feasible techniques are still unavailable.

This workpackage focuses on design of innovative low cost methods for remediation of sites, where past and present contamination from metal industry can be found. Furthermore the workpackage concentrates on classification of present and future mining activities, in order to prepare integrated plans for long-term protection of environment at a local level.

WP5 – Risk assessment and advanced chemical methods for remediation of soils contaminated by hydrophobic organic pollutants.

1) The first purpose of this workpackage is the correlation of the database (WP1) to physical, chemical and biological treatments developed during the project (WPs 1 to 5). In addition, acceptable limits of efficiency of the processes for different classes of pollutants must be identified using risk assessment and available data about sites.

2) Use of natural highly-biodegradable surfactants for removal of hydrophobic organic pollutants. This will possibly be a pre-treatment for highly persistent and toxic compounds like dioxins, polychlorobiphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). This pre-treatment will then be followed by the remediation techniques developed in other workpackages.

Finally, the project will possibly yield an advanced tool for environmental management, thanks to the coupling of the database with the risk assessment. Final result should be a standard protocol for remediation of polluted sites.