Environmental Science and technology

introduction

The Program on **Environmental Science and Technology** developed at the Chemical and Environmental Technology Center comprehends environmental chemistry (water, soil and atmospheric chemistry), clean technologies (desulfurization of diesel and oil, biodegradable polymers and structural modification of polymers, recycling, pyrolysis of dangerous chemicals by molten salt technology), nanotechnology (magnetic nanoparticles, dendrimers, nanobiomarkers, catalysts) and chemical characterization of nuclear fuel and nuclear fuel cycle waste (chemical and isotopic characterization).

The Chemical and Environmental Technology Center was established in 1995, as an evolution of the former Department of Chemistry Engineering (1970). The program on environment science and technology was structured as consequence of the continuous growth of environmental activities on areas related to nuclear programs of IPEN. Moreover, it was an answer to the society concerning the climate changes and biodiversity preservation.

All activities of research and development, services, supervision of graduate and under graduated students and courses performance at the center were related to the development, improvement and establishment of new technologies. The highlights of this period (2011 - 2013) were:

- Development and use of modern analytical technology for the characterization of persistent pollutants and endocrine disrupters (metals, PAHA's, PCBs, Pesticides, hormones, surfactants, plasticizer and human pharmaceuticals) in order to evaluate water quality and/or sediments;
- Atmospheric chemistry and greenhouse gases: Evaluating an estimation of surface trace gas fluxes from aircraft measurements above the Amazon;
- Cooperation with SABESP (Water and Sewage Company) and CETESB (State Environment Agency) in program for the development of public policies;
- Studies and development in biodegradable polymers, polyolefins and advanced methods for polymer and rubber recycling and re-use;
- Studies and development of recycling technology re-use of materials, waste storage and decontamination;
- Clean technologies: Safe decomposition of organohalogenated pesticides by molten salt oxidation;
- Synthesis and development of magnetic nanoparticles, biosorbents, nanobiomarkers, zeolites and ceramics applied to environmental monitoring and wastewater treatment;
- Establishment of procedures and techniques for nuclear forensic investigations;
- Certification and maintenance of the Quality Management System - ISO 17 025;
- Environmental monitoring program (EMP-Q) to assist the nonradioactive chemical at IPEN;
- Non-radioactive chemical waste disposal program.

These achievements were conducted with support from national and international funding agencies - FAPESP, CNPq, FINEP/MCT, CAPES, IAEA; NOAA; NERC; NASA as well as cooperation with partners and clients, such as SABESP, CETESB, INPE, INPA, USP; Braskem, Biolab Sanus and Petrobrás.

Environmental chemistry and water science

The global importance and vulnerability of our water supply, both in terms of quantity and quality has been well documented and, although water is a renewable resource, it is also a finite resource. Water, vital to both human health and ecosystem sustainability, is under increasing pressure as urbanization and agricultural intensification increase and, as such, it is essential that we improve our understanding of the types, and complexity and potential impacts of chemicals that are increasingly being released into the environment.

It is recognized that the pollution influences living organisms, humans included, both directly (by affecting their health) and indirectly (via contamination of food and abiotic compartments). Heavy metals and organic compounds, such as poly aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs) and pesticides, have been the center of attention for a long time.

Environmental and Analytical Chemistry focus activities in these areas by bringing together academic staff with a common research interest in understanding a variety of aspects of natural and polluted present-day environments and ancient environments. Since these are complex systems, studies of both organic and inorganic species of natural and anthropogenic origin rely heavily on the use and development of modern analytical methods. Scientific Cooperation programs supported by CNPq and FAPESP in partnership with Environmental Agency State (CETESB) and SABESP were developed.

Historical reconstruction of the pollution Guarapiranga Reservoir and diagnostic of sediment quality of São Paulo Metropolitan Region (SPMR) water supply reservoirs facing their management (thematic project set with Botany Institute)

Freshwater is a natural resource that has been under strong pressure, to the point of becoming one of the greatest XXI Century threatens. Under this water crisis context, the São Paulo Metropolitan Region (SPMR) is emblematic. This research will adopt innovative approaches that consist of the paleolimnology-neolimnology integration, as well as of the use of antropogenic impact multi-proxies. It is based on three main approaches: (a) evaluation of the eutrophication process evolution and the historical antropogenic impacts of Guarapiranga Reservoir (1906/2009-present); (b) characterization of multi-proxies present in recent sediments of 30 reservoirs circumscribed in the SPMR water supply area; and (c) integration of approaches (a) and (b) to elaborate a diatom-phosphorus inference model that will allow estimation of the past phosphorus levels of the Guarapiranga Reservoir water, as well as the positioning of the other reservoirs along the trophic gradient reconstructed.

Paleolimnology will include the reference levels (before impact) of Guarapiranga Reservoir, and will be evaluated by ^{210}Pb dated sediment core. Neolimnology will include variables collected from the water column and superficial sediments of 30 reservoirs (20 water supplying ones). Multi-proxies will include eutrophication bioindicators (diatoms), granulometry, organic geochemistry (TOC, TP, TN, ^{13}C, ^{15}N) and sterols, geochemistry of persistent pollutants (metals, PAHs, PCBs, pesticides, hormones, surfactants and a plasticizer). Elaboration of the inferential model will be accomplished by using quantitative diatom species distribution in water and recent sediments. Watersheds of reservoirs will also be analyzed concerning physical environment (geology and geomorphology) and also land use and occupation. Above information will contribute towards the proposition of targets to support recovery and/or conservancy, and the elaboration of environmental scenarios, providing innovative subsides for the SPMR water supply reservoir management. The Laboratories of Chemistry and Environmental Diagnosis Center will conduct the analysis of metals and organic compounds evaluating endocrine disrupters in the samples colleted.

Environmental monitoring of emerging pollutants, drugs, endocrine disruptors and organic markers in water for public supply on the Guarapiranga dam, Brazil

The focus of this research is investigating the presence of some endocrine disruptors agents used as personal care, pharmaceuticals and industrial products which may affect the water quality of public supply. The Guarapiranga dam is the second largest producer of drinking water in the metropolitan region of São Paulo and supplies around four million inhabitants. Located in an urban region has suffered environmental impact on water quality due mainly to the release of untreated sewage from the disorderly occupation of their surroundings.

Evaluation of endocrine disruptors in water for public supply on the Guarapiranga dam, Brazil. Development and validation of analytical methodologies

This study aim is develop and validate analytical methodologies to determine some compounds considered endocrine disruptors or organic markers of anthropic degradation influence in water, for public supply effluents which may have been dumped in the municipal waters from sewage treatment plants. Personal care products and others potential endocrine disrupters are part of a large and diverse group of organic compounds labeled as emerging contaminants. Several chemical substances suspected of acting as endocrine disruptors are currently being used in industrial and agricultural activities in Brazil, but the hormones and pharmaceuticals stand out because they are potentially active compounds in biological systems and are related to the origin of several types of cancers. The effects of these endocrine disruptors to human health are not totally known, then it's necessary to implement a national program to evaluate such impacts. Scientific cooperation programs supported by CNPq and FAPESP in partnership with SABESP and the Institute of Botany have been developed with this focus. Applying the validated analytical procedures on the samples from Guarapiranga Dam, some compounds have being detected at raw and drinking water, principally during to drought season. In this research it was used solid phase extraction technique (SPE) for extraction and concentration of samples, followed by gas chromatography coupled to mass spectrometry, GC/MS, for identification and quantification of organic compounds.

Occurrence and distribution of pharmaceuticals in the waters of Guarapiranga dam, SP, Brazil. Development and validation of methodology

The objective of this study is to assess the occurrence and distribution of pharmaceutical in the waters of Guarapiranga dam, SP, Brazil. After ingestion, the majority of human pharmaceuticals are excreted in urine and feces via the sewage treatment network. The occurrence of these substances in aquatic environment is due primarily to inefficiency of conventional procedure (coagulation, and filtration) of the STPs that are unable to totally remove them. As a result, in the last decades, many researchers have reported the presence of pharmaceuticals in sewage treatment plant (STP) influent/effluent, sea water, surface water, and, exceptionally, in the drinking water.

A methodology for the determination and quantification of 23 human pharmaceuticals using solid phase extraction (SPE) combined with liquid chromatography electrospray ionization-high performance mass spectrometry (LC-ESI-MS/MS) was developed and validated.
The analysis results have shown two areas of greatest impact that coincide with the region of highest occupancy around the dam. The higher concentration of caffeine in these areas suggests the occurrence of direct discharge of domestic sewage into the dam waters. The application of the method conducted an environmental assessment of the levels of pharmaceuticals compounds in water for public supply. This study is part of the Thematic Project FAPESP-nº 2009/5389-9, in partnership with Institute of Botany and SABESP.

The historic profile of eutrophication in the Reservoir Guarapiranga

Guarapiranga Reservoir is the second most important public water supply in São Paulo, Brazil, and has been eutrophic for several decades. We inferred the major ecological shifts for the period 1919-2010 related to multipli stressors (forest flooding, hydrological change, use of algicide end eutrophication) using geochemistry in a short (75-cm) sediment core. Diatoms and geochemical variables show that the reservoir was oligotrophoc from ~ 1919 to ~1947. Eutrophication began ~ 1975 and by the early ~ 1980s the reservoir increase in human population in the watershed. Several cultural eutrophication has persisted since ~ 1990. Higher concentrations of copper in sediments, beginning in 1991, reflect the increased use of copper sulfate to control cyanobacteria blooms and provide a chronological maker.

Evaluation of environmental impact on Pedroso Dam, Santo André, Brazil, by the construction of the beltway. Distribution of polycyclic aromatic hydrocarbons, PAHs, metals and trace elements in sediments and waters of region

This project research aims to evaluate the environmental impact on the study region, characterizing water and sediments of the reservoir before and after the beltway construction to compare the actual and initial quality of this water resource. It was analyzed the potential risk of contamination by polycyclic aromatic hydrocarbons (PAHs) in sediments and water, examining the main compounds from air pollution caused by motor vehicles that circulate in the region. An environmental diagnostic to identifying the presence of PAHs in sediment and surface water was carried out. The investigation of impact agent presence which can contribute to impoverishment of the Reservoir Pedroso quality was realized, aiding the management plan for water resources of the Santo André city. The “Park Pedroso” reservoir is an area of Integral Protection Conservation, situated in the area of Billings basin, main potability water source of MRSP. The area is rich in water resources, but has poor infrastructure. The Park Pedroso reservoir provides about 7% of drinking water in the city (54.3 million liters of water). In this research it was used ultrasonic extraction and solid phase extraction (SPE) for extraction and concentration of samples, followed by liquid chromatography coupled to UV visible, HPLC, for identification and quantification of PAHs compounds.

Physical and chemical aspects of Paraibuna and Paraitinga Reservoirs complex, São Paulo

Water is a natural resource, essential to life, and its quality, an important feature to evaluate the possibilities of its use. This study aimed to evaluate the water quality of the Complex Paraibuna-Paraitinga, classified as Class 2 water body, located in the basin of Paraíba do Sul River, State of São Paulo. In order to analyze the water quality of these reservoirs, this paper presents an analysis of some limnological parameters: air temperature, water temperature, electrical conductivity, dissolved oxygen, pH, transparency, turbidity and total solids; the concentrations of anions: nitrate, fluoride, sulfate, phosphate and chloride; and concentrations of trace elements: Hg, Se, As, Sb, Pb, Cd, Ag, Al, B, Ba, Be, Co, Cr, Ca, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Si, Sn, Sr, Ti, V and Zn, obtained from samples of surface water, middle and bottom of water column, representing eight sampling stations. The results were compared with the limits established by CONAMA Resolution 357/2005. From the 30 elements analyzed, only aluminum, iron, phosphorus, silver and manganese concentrations were above the legal standards, especially in rainy periods. The limnological parameters were within the standards for oligotrophic environments, such as these reservoirs are classified. The ionic species present most results below the quantification limits and under the legislation. From the results obtained, it appears that the reservoirs Paraibuna and Paraitinga are preserved, and are free of contamination by metals and trace elements, suggesting that the concentrations of Al, Fe, P, Ag and Mn are linked to the geological feature of the region.

Water quality evaluation of the Taquaruçu Grande sub-basin and its interference area in the reservoir of the Luis Eduardo Magalhães hydroelectric power station - To, Brazil

This work aimed at verifying the physical, chemical and biological contribution of the Taquaruçu Grande sub-basin to the reservoir of the Luís Eduardo Magalhães hydroelectric power station, in the medium Tocantins - TO, Brazil. Data were collected quarterly in the rainy and dry periods from January 2007 to October 2008, in eight points located in the sub-basin and in the reservoir. Limnologic variables were colleted and analyzed in accordance with CETESB (2006) and APHA (2005), as well as metals and trace elements analyzed by inductively coupled argonium plasma (ICP-OES) - atomic absorption spectrometry (AAS) with graphite furnace or hydride generation. Biologic samples were collected with 20 μm plankton net, fixed in Transeau’s solution (proportion 1:1) for qualitative analysis and in acetic Lugol’s solution for the quantitative analysis made in a Olympus BX41 microscope.

Electric conductivity, water temperature, total dissolved solids, phosphorus and pH showed higher concentration in the lentic points than in the sub-basin, with higher parameters in the rainy period, which is attributed to the amount of allochthonous matter carried by the rain to the reservoir. Nitrate and fixed solids show higher concentration in the reservoir in the dry period. Eutrophycation conditions have become more intense with the rise of the dry weather and can be a consequence of organic matter decomposition processes, which release nitrogen compounds. The higher concentration of fixed solids in the dry period is probably related to the low depth of the points, which favors the re-suspension of sediments by the action of winds and local hydrodynamics. Ba, Na, Si, K, Al, Mn, Zn, Li, Mg, P, Ca, Fe and Ag were present in all points in most of the sample period. Samples from October 2007 presented high concentrations of B, Al, Cr, Ni, Cu, Zn, Mo, P, Co and Ag mainly in the sample points of the sub-basin, associated to the low depth of the streamlets, which in this period shown shallow water favoring weathering. Al, Ag, Be, Co, Cr, Cu, Fe, Mn Mo, Ni, P and Zn presented samples in discordance with CONAMA 357. The phytoplankton was characterized by presenting 227 taxons, 95 genus, distributed in 13 taxonomic classes. It was observed a spatial variation of species richness, with a lower number of species in the microbasins due to lotic conditions of these places, and a higher number of taxons in the reservoir. High stability of the water column and elevated nutrient availability propitiated an expressive phytoplankton development in the lentic points similar in composition and density.

Water quality of the Taquaruçu Grande stream, as well as patterns of distribution of cyanobacteria and cyanotoxins - To, Brazil

Situated in the middle Tocantins, the reservoir Luiz Eduardo Magalhães, known as UHE Lajeado, represents the most viable source of supply to the town of Palmas. For that was instituted a monitoring program, which lasts three years, aiming to better understand the water quality of the Taquarussu Grande stream, as well as patterns of distribution of cyanobacteria and cyanotoxins. The study sought to understand the spatial and temporal dynamics of cyanobacteria and cyanotoxins through monthly assessments between 2006 and 2008, verify correlations between points upstream and downstream to the main point studied, and propose using the diagram of water treatment technology feasible. For this, samples were taken at 1 Point, predetermined point of captation as possible, the 3 Point, downstream, and RT point, upstream. The results showed that total nitrogen and phosphorus has practically defined the patterns of distribution of cyanobacteria. We detected the formation of three cyanobacterial blooms in 1 point, and is evidenced concentrations above 2.0 $\mu g.L^{-1}$ of microcystins in 1 and 3 Point. Overall, the results suggest a systematic evaluation of these toxins and their potential producers in the points assessed.

Assessment of environmentally available metals in sediment samples from water for public supply of the city of Palmas, Tocantins

The sediments are an important tool for assessment of aquatic ecosystems quality, for indicating the presence of contaminants released continuously into the environment as a result of human activities. Among chemical substances discharged to surface water, there are metals that in undesirable amounts, can be toxic to biota. Due to the importance of sediment and of shortage of data of water quality of the Araguaia-Tocantins river system, the present study conducted an assessment of environmentally available metals in sediment samples from water for public supply of the city of Palmas, in Tocantins, Brazil. The concentrations of As, Cd, Pb and Se were analyzed by Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Ag, Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Sb, Sc, Si, Ti, V and Zn were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Hg by Cold Vapor Atomic Absorption Spectrometry (CVAAS). Two partial solubilization processes were performed for a comparative study, one with HCl 0,1 M and agitation at room temperature, considered a milder method for metal extraction from anthropogenic origin, and another with HNO_3 8 M and microwave heating, considered as an alternative to more complex methods of total digestion, since it provides a good evaluation of the total concentration of the elements. The sediment quality evaluation was realized by comparing the concentration values of the elements As, Cd, Cr, Cu, Hg, Ni, Pb and Zn with the quality guidelines (TEL and PEL) adopted by *Canadian Council of Minister of the Environment* (CCME), to thereby provide a better monitoring of the water quality of the Araguaia-Tocantins river system.

Determining properties of absorption, distribution, metabolism and elimination (ADME) of the active Swertisina by LC-MS/MS

The goal of this study is to determine the biopharmaceutical properties (ADME in vitro) of the chemical entity 2"-O-raminosil swertisina (SWOR) extracted from *Aleurites moluccana*. The Aleurites exhibits therapeutic potential against inflammatory processes by inhibiting both the vascular and cellular events. It is important to have knowledge of the ADME properties in the earlier drug development stages to take rational decision and direct the project to succeed in later stages. The SWOR showed high solubility and stability, low absorption, low plasma protein binding and low metabolic rate, with no metabolite identified. The LC-MS/MS technique was applied as analytical tool.

Environmental monitoring program (EMP-Q) to assist the non radioactive chemicals at IPEN

IPEN has implemented an Environmental Monitoring Program since 2007, which has as main objective the life and property safety in its plant of 478,000 m^2. As a research and production facility, many chemical, biological and radioactive products are manipulated in its laboratories. To assure that no hazardous substances were released to the environment, the program analyses stable chemical compounds in the groundwater and wastewater generated by the institute. Annually, the program performed more than eight hundred analyses, including pH, temperature, total and dissolved solids, metals (Al, Sb, Ba, Cd, Pb, Co, Cu, Cr, Hg, Mo, Ni, Ag, Na, Zn, Ca, Mg, Be, Sn, Li, K, Sr, Ti and V), semimetals (As, B, Se and Si) and anions (chloride, nitrate, sulfate and fluoride).

Wastewater
Wastewater aliquots were collected daily at a Monitoring Station installed in the north entrance of the institute, according to nationally recognized sampling references (CETESB, 1987). The obtained results were compared to the values established by Brazilian laws for releasing of effluents in domestic sewer system. Currently the effluent released from Ipen is compliant with legal guidelines values established by São Paulo 8468 state law (article 19-A).

Ground water
In order to assure that IPEN's activities do not lead to groundwater resources contamination, the environmental program includes chemical quality evaluation of six monitoring wells installed in different areas of the institute. The program so far showed there is no evidence of contamination by the evaluated compounds in IPEN's ground waters. Currently the environmental monitoring program has the following aims:
- To assess the environmental impact from activities of IPEN;
- To keep systematically records from natural levels of stable chemical compounds, in the influence area of IPEN;
- To improve the current sampling, preparation and analysis protocols;
- To detect any potential flaw on environmental safety and plan corrective measures;
- To provide information to the general public.

Non-radioactive chemical waste disposal program

Environmental issues are a major concern for the institution. Despite the Brazilian laws, IPEN has implemented a Chemical Waste Disposal Program dealing with the non-radioactive chemical wastes following the ideas stated in its Mission. Residuals are yielded in the several processes even running routinely or in the periods of a variety of researches, or also due to expired reagents. These materials are identified, classified and kept in temporary vessels until final disposal. Proper training is provided to internal technical personnel in order to equalize procedures and actions. The management of the information is carried out using an internal computer network to input data and visualize details and exchange items. The benefits of this policy are: cleaner and safer areas, organized work place, lower environmental risks, reduced budget for management of remaining items, and environmental laws and regulations compliance. All these wastes are sent to disposal in accordance to technical norms and Brazilian and local laws and regulations. One of the most significant goals was the understanding by the internal community that the residual is a consequence of our acts and a proper behavior can make living and working easier and safer.

Toxic elements mobility in soils with coal fly ash columns and ecotoxicity of columns leachate

The experimental part (columns preparation and leaching) of this study was described in progress report 2008-2010 and the results showed that As, Cd, and Mo were leached from Figueira coal fly ash with acid solution in long-term leaching and Zn was not much leached and Pb was not leached. Leached Cd from coal fly ash was the element more retained by clay soil and sandy loam soil followed by As. Leached Mo from coal fly ash was not detected in soils and leachates of soils with coal fly ash columns because of concentration this element was below the quantification limit of method. Leached As and Cd from coal fly ash changed the soils quality because the concentration of these elements in soils was above intervention value and quality reference value established by the Environmental Protection Agency of the state of São Paulo (CETESB), respectively.

To supplement this study the ecotoxicity of coal fly ash leachates and leachates of soils with coal fly ash columns was evaluated by tests using *Lactuca sativa* (Figure 1) and *Daphnia similis* (Figure 2) as organisms. According to results were observed toxic effects to seed germination of *Lactuca sativa* and to mobility and/or survival of *Daphnia similis* in coal fly ash leachates. The leachates of soils with coal fly ash columns not presented toxicity to both organisms indicating that the soils retained toxic substances leached from coal fly ash and this is according to concentration of As and Cd in soils described previously.

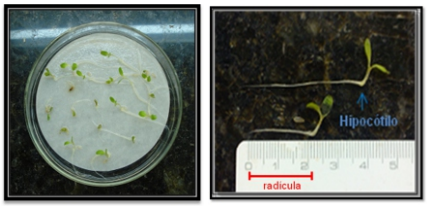

Figure 1. Seed germination and root elongation test with *Lactuca sativa* organism.

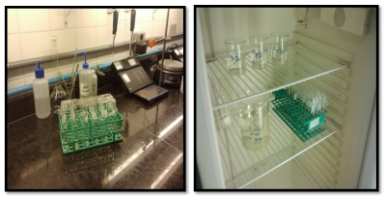

Figure 2. Acute toxicity test with *Daphnia similis* organism.

Ecotoxicological effects of pharmaceuticals and insect repellents products in the aquatic organisms

Dipyrone and paracetamol were study on different freshwater organisms. The lethal effect was determined by acute toxicity assays with *D. similis*, *C. dubia*, *C. silvestrii* and *Danio rerio*. The sublethal effects were determined by embryotoxicity with *D. similis* embryos at 20°C and chronic toxicity with *D. similis*, *C. dubia* and *C. silvestrii*. The LC(I);96H to *Danio rerio* was 3.670mg.L^{-1} and 590mg.L^{-1} for dipyrone and paracetamol, respectively. Dipyrone and paracetamol induced malformations in *D. similis* neonates and embryos and the IC50 obtained was 21.1mg.L^{-1} and 94mg.L^{-1} respectively. Values of IC50 to *C. dubia*, *C. silvestrii* and *D. similis* on individual chronic toxicity tests with dipyrone was 5,98 and 3.57, 21.84 mg.L^{-1} respectively. The IC50 to *C. dubia* and *C. silvestrii* in individual chronic tests with paracetamol was 7.24 and 4.15 mg.L^{-1} respectively. The IC50 obtained to *D. similis*, *C. dubia* and *C. silvestrii* for Dipyrone was 8.84; 10.82; 4.68 and 2.81mg.L^{-1} respectively. For chronic population tests with paracetamol the IC50 to *D. similis*, *C. dubia* and *C. silvestrii* was 9.57; 6.48 and 4.26mg.L^{-1} respectively. According to the classification based on the European Directive 93/67/EEC, these compounds are hazardous to the environment.

Ecotoxicological effect of insect repellent active ingredients on aquatic invertebrates was studied utilizing irradiated (gamma rays) and non-irradiated organisms test. DEET (*N,N-diethyl-meta-toluamide*) is the active ingredient used in most insect repellents. DEET is an environmentally persistent compound and has been proven its toxicity to some aquatic organisms. The lemongrass essential oil, one of the most used in order to replace synthetic products, has no study proven its toxicity to aquatic biota. In addition to chemical pollutants, aquatic organisms may be exposed to ionizing radiation from natural sources (background radiation) or near nuclear installations. It was evaluated the in vitro cytotoxicity as well as acute and chronic ecotoxicity of DEET and lemongrass oil on *D. similis* and *C. silvestrii* irradiated and non irradiated organisms. The cytotoxicity index ($IC_{50\%}$) for essential oil was about 50 mg.L^{-1} and 420 mg.L^{-1} for DEET. The acute toxic effect on survival (EC50) on *D. similis* for essential oil was 7.2 mg.L^{-1} and 64.9 mg.L^{-1} for DEET and on *C. silvestrii* was 3.8 mg.L^{-1} for essential oil and 53.9 mg.L^{-1} for DEET. The reproduction inhibition concentration (IC25) on *C. silvestrii* was 3.4 mg.L^{-1} for essential oil and 16.4 mg.L^{-1} for DEET. The gamma radiation lethal dose (LD50) for *D. similis* was 242 Gy and 525 Gy for *C. silvestrii*. The *C. silvestrii* reproduction decreased by 25% at 29 Gy dose. *C. silvestrii* were irradiated at 25 Gy and were submitted to acute ecotoxicological test with the active ingredients. The results showed that the *C. silvestrii* reproduction was not significantly affected after gamma irradiation compared with non-irradiated organisms.

DEET is considered an emerging pollutant and studies indicate that it is only slightly toxic to aquatic organisms. There are not complete assessments for ecological risk of DEET, including studies evaluating chronic toxicity to aquatic organisms. So the DEET toxicity was also evaluated by the effects caused on lysosomes of *Perna perna* mussels hemocytes on irradiated and non-irradiated organisms. For this purpose, assays were performed to identify the acute toxicity of DEET concentration and the gamma radiation lethal dose. Subsequently, cytotoxicity assays were carried out to assess the stability of the lysosomal membrane in organisms exposed to ionizing radiation and DEET. The obtained result in acute toxicity test was LC50 = 114.27 mg L^{-1}, and the radiation lethal dose (LD50) was 1068 Gy. In the cytotoxicity assay the result of non-observed effect (NOEC) for irradiated and non-irradiated organisms was 0.0001 mg L^{-1} and of observed effect (LOEC) at concentrations above this. The IC25 (72h) for non-irradiated organisms was 0.0003 mg L^{-1} and IC50 (72h) was 0.0008 mg L^{-1} for irradiated and non-irradiated organisms. Despite of DEET concentrations which cause effect found in this study were higher than in the environment, both measurements are in the same order of magnitude and should be also take into account the possible synergistic effects of DEET with other contaminants in the aquatic environment. The cytotoxicity assay obtained results showed that DEET demonstrated cytotoxicity effect to the *Perna perna* mussels in all the tested concentrations.

Resveratrol is considered to be a cell protector with radiomodifying effect. The study was carried out on culture of human rhabdomyosarcoma cells (RD) by applying the comet assay to evaluate the cell damage and repair capacity. The LD50 obtained was 499.95±9.83 Gy (Mean±SD) and the CI50% was 150 µM in the RD cells. Based on these data, it was defined the gamma radiation doses (50 and 100Gy) and resveratrol concentrations (15, 30 and 60 µM) to be used in this assay. The cell damages obtained in this study are classified visually by the intensity of fragmentation of the nucleoids into five categories (0 - IV), according to the criterion established by Jaloszynski et al. and Mozdarani et al. and presented in Fig. 3. The results indicate that resveratrol acts as a cell protector at a concentration of 15 µM and has a cytotoxic effect at 60 µM. However, with the interaction of the gamma radiation, the concentration of 60 µM did not produce a statistically significant radiosensitizing effect.

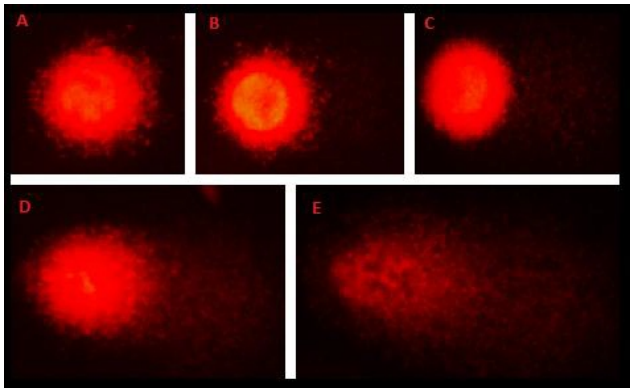

Figure 3. Micrography of RD cells: visual classification of comets: (A) comet class 0; (B) comet class I; (C) comet class II; (D) comet class III and (E) comet class IV.

Atmospheric chemistry

Modifications by anthropogenic pollution of the natural atmospheric chemistry and particle microphysics of the tropical rain forest during the GoAmazon (Green Ocean Amazon)

The GoAmazon campaign seeks to quantify and understand how aerosol and cloud life cycles in a particularly clean background in the tropics are influenced by pollutant outflow from a large tropical city, all in the context of addressing the susceptibility of cloud-aerosol-precipitation interactions to present-day and future pollution in the tropics. Within this context of GoAmazon, the overall goals of the proposed research are (i) to measure and mechanistically understand the factors affecting the number-diameter distribution *n(d)* of the atmospheric particle population over a tropical rain forest (especially the effects of anthropogenic pollution as a perturbation to natural state) and (ii) to develop and implement an upscaling analysis from this new data set and knowledge of *n(d)* to prognosticate possible climatic impacts of present-day urban pollution and possibly greater pollution in the future. In relation to these goals, the proposed project has three objectives, as follows:

The **first objective** is to understand and quantify the interactions of biogenic and anthropogenic emissions with respect to the production of secondary organic aerosol. Hypotheses to be tested are that (i) a shift takes place under anthropogenic conditions in the fate of organic peroxy radicals from HO_2 to NO pathways (to be tested by gas-phase analysis by CIMS and PTR-MS; leading to altered rates of particle

growth (to be tested by number-diameter distribution measurement of MAOS and AAF, (ii) a significant increase occurs under anthropogenic conditions in the total potential material that can ultimately condense after atmospheric aging to the particle phase (to be tested by the data set of the oxidation flow reactor; as well as in chemical composition that can influence optical properties and CCN activity (to be tested by the data sets of MAOS, and (iii) these significant changes in the atmospheric particle population can be monitored regionally by satellite.

The **second objective** is to understand and quantify the mechanisms of new particle production over the tropical rain forest, both for natural and anthropogenically influenced conditions. Hypotheses to be tested are that (i) new particle formation occurs above the boundary layer (to be tested by aircraft observations of number-diameter distributions, (ii) new particles are produced from the evaporation of the jet droplets from fungal spore emission (to be tested by nanoparticle analysis for potassium by the TDCIMS, and (iii) an absence of sufficient H_2SO_4 concentration in the gas phase explains the differences for Amazonia compared to other observational sites worldwide (to be tested by gas phase analysis for H_2SO_4 by CIMS. These hypotheses will be separately evaluated for conditions when the research site T3 is under influence or not of the plume from Manaus (i.e., natural compared to anthropogenically influenced conditions).

The **third objective** is to translate the new microphysical knowledge into a refined quantitative understanding of the links to climate. Hypotheses to guide the proposed upscaling analyses are that (i) microphysical modeling coupled with aircraft and ground site observations can prognosticate and validate the anthropogenic influence on cloud-aerosol-precipitation interactions associated with the Manaus plume and (ii) satellite-based products can be validated by in situ observations and subsequently used to provide a quantitative assessment of the regional effects of Manaus pollution (e.g., such as on direct and indirect radiative forcing, air quality, and human health, with a focus of the funded study on the first of these three.

The proposed activities and associated three objectives, when taken together as a whole, respond to the Thematic Area of Atmospheric System Research (ASR) of DOE DE-FOA-0000919, FAPESP Chamada FAPESP 21/2013, and FAPEAM EDITAL N. 013/2013. With respect to Science Areas of those calls, the proposal will “improve understanding of the life cycle of aerosols including the interaction of pristine and polluted air masses” (80% of proposed effort) as well as “improve understanding of the interaction of aerosols and clouds over the Amazon basin, including aerosol impacts on precipitation as well as cloud impacts on aerosol transport, chemistry, and removal” (20% of proposed effort).

Study of atmospheric chemistry using the relaxed eddy accumulation technique

Relaxed eddy accumulation is a conditional sampling technique used to measure the exchange of chemical species between the atmosphere and terrestrial sources or sinks (vertical flux). In this technique a compact system designed to segregate air based on the direction of the instantaneous vertical wind velocity is used to sampling. The air samples basically are accumulated in two storage reservoirs, one for upward moving air and one for downward moving air. The advantage of this system upon others is that it was made to be low cost, low power and robust. The system is although designed to sample air onto absorbent cartridges. The air sampler consists of solid absorbent cartridges, preceded by an ozone O_3 filters, a sample pump, flow sensor and a commercial microcomputer, which monitored flow through the cartridges. Finished the sample procedures the cartridges need to be desorbed by a custom thermal desorption system directly into a GC/MS.

Amazon green house gas balance studies in Amazon basin using vertical profiles with small aircraft

This project is part of the LBA project (Large-Scale Biosphere-Atmosphere Experiment in Amazônia) in December 2000, with vertical profiles of CO_2, CH_4, CO, H_2, N_2O and SF_6 over Tapajós National Forest, a primary forest in Para State - SAN (Santarém). In January of 2010 started new project: a consortium of many international institutions, entitled: AMAZONICA, coordinated by Dr. Manuel Gloor, from University of Leeds, funded by NERC (National Environmental Research Council - UK), were IPEN/LQA (Atmospheric Chemistry Laboratory) received £ 510K to perform vertical profiles in a big box over Amazon basin to represent the entire Amazon Basin. The aircraft sites added to SAN were: Rio Branco, Acre state (RBA), Tabatinga, Amazonas state (TAB) and Alta Floresta, Mato Grosso state (ALF) (Figure 4). In the coast, it were added more 2 sites: Salinópolis, Pará state (SAL) and Natal, Rio Grande do Norte state (NAT).

Figure 4. Amazon aircraft sites (yellow aircrafts), white markers coast flasks sample and ASC and RPB Island from WMO network used in the study.

Samples are collected aboard light aircraft between the surface (300 m) and either 4.4 km (SAN, RBA, TAB and ALF) using the NOAA/ESRL/GMD (National Oceanic Atmospheric Administration/ Earth System Research Laboratory/ Global Monitoring Division) semi-automatic Portable Flask Package (PFP). The PFP consists of 17 (SAN) and 12 (RBA, TAB and ALF) glass flasks with 750 mL volume that are pressurized to about 3 bar to enable measurements of all the gases mentioned above. The analyses were made at IPEN/CQMA/LQA that is a replica of the NOAA laboratory trace gas analysis system. It was constructed and installed in IPEN/LQA starting in May 2004. The equipment set up in Brazil is capable of high-accuracy and high-precision measurements of CO_2, CH_4, CO, N_2O and SF_6 in the flask and PFP samples. All measurements are calibrated with standards from NOAA to internationally accepted scales. The fluxes are determinate for each profile by Integration Column Technique using atmospheric measurements from aircraft profiles over the 4 sites (SAN, RBA, ALF and TAB) subtracted with background concentration of air when cross the Brazil coast. The CO_2 background was determinates using a co-measured SF_6 as a transport tracer. Two NOAA/GMD background sites, Ascension Island (ASC) located in the Atlantic Ocean (8’S, 14’W) and Barbados (RPB) located in the Atlantic Ocean (12’S, 59”W) were used to calculate the fractions of air arriving at the sites studied. The fluxes are related with the time that air mass take between coasts until profile sites. Back trajectories from HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectories) model were calculated for every profile each 500 m height to determinate the time of the air mass between coast and the sites (Figure 5).

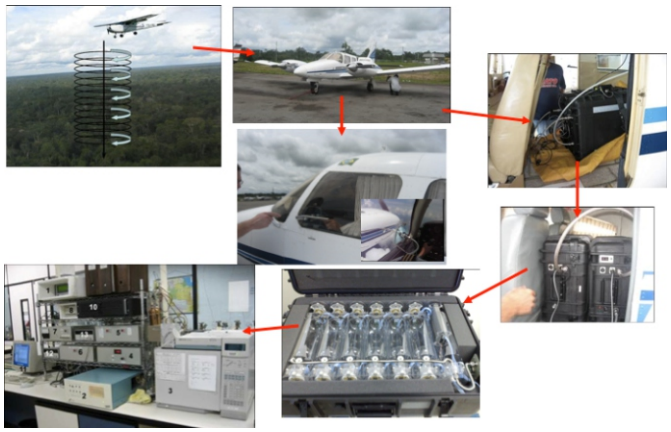

Figure 5. Sample and analyze sequence showing descendent spiral profile, inlet installation in the aircraft widow, equipment installation in the aircraft, portable Flask Package and the Green House Gas Laboratory in the LQA/CQMA/IPEN.

This measurement program started in January of 2010 until the present, and was performed around 80 profiles per year, almost 2 per month per site. The collaboration with Dr. John Miller (NOAA) and Dr. Manuel Gloor formed many students specialized in Amazonian studies related with GHG and climate change (3 pos-doc, 2 doc, 4 master degree) and produced a Nature paper, published at 6/feb/2014 and more 7 others since 2010. Financing by NERC, FAPESP, 7Framework Program Europian Community, MCTI/CNPq, CAPES, NASA, NOAA and IPEN.

Polymers and environment

Polymeric hydrogels with silver nanoparticles for medical applications

In the whole world, an increasing interest in the use of hydrogels as dressings for burns, wounds and skin ulcers has been observed, considering that they are capable of absorbing exudates, aiding in healing , and providing comfort to the patient since they favor his pain relief. In addition, hydrogels can also be applied as matrices for controlled release systems of active and antimicrobial agents. The use of ionizing radiation in attainment of hydrogels enables simultaneous cross-linking and sterilization, that is, the synthesis of a product not contaminated with toxic residues. Moreover, it also enables, *in situ*, the synthesis of silver nanoparticles (AgNPs) inside the hydrogels from $AgNO_3$ dissolved in the corresponding polymeric solutions without the use of catalysts or other reagents to obtain medicinal dressings with antimicrobial action. Noteworthily, AgNPs exhibit excellent antibacterial property and also show to be favorable in reducing local inflammatory response facilitating the healing of wounds.

Results: Hydrogels from poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) have been obtained with different plasticizers and polysaccharides, and around 40 ppm of AgNPs per each formulation of them. The resulting membranes with different physical and chemical properties were obtained after γ-irradiated at a dose of 25 kGy. Fig. 6 shows one of the obtained hydrogels.

Figure 6. Hydrogel of poly(*N*-vinyl-2-pyrrolidone).

Figure 7 shows spectra of hydrogels PVP / PEG / agar and PVA / KC / agar exhibiting peaks of plasmon absorption band at λ ~ 403-405 nm and suggests that there was formation of spherical particles.

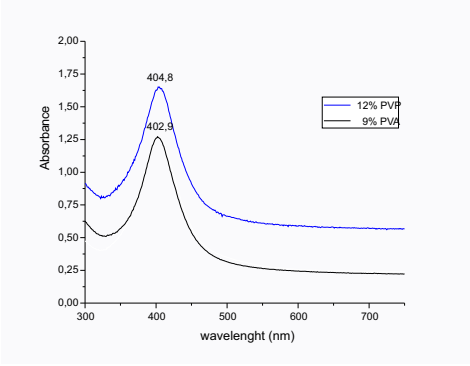

Figure 7. Plasmon resonance spectra obtained from hydrogels of PVP / PEG / agar and PVA / KC / agar.

Hydrogels with AgNPs showed antimicrobial activity against *gram-positive* and *gram-negative* bacteria, including a strain of *S. aureus*, multi-resistant against penicillins, cephalosporins, carbapenems, sulfonamides, tetracyclines, quinolones, and aminoglycosides. Fig. 8 shows results obtained for gram-positive and gram-negative bacteria.

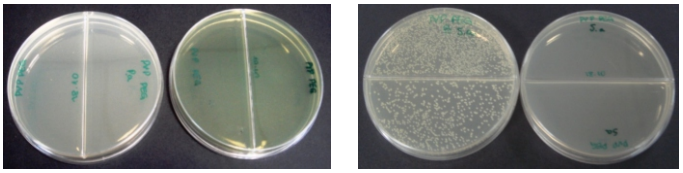

Figure 8. The results obtained in the evaluation test for microbial activity of PVP / PEG / agar hydrogel against (A) *P. aeruginosa* and (B) *S. aureus*.

Silver ions can be reduced efficiently by gamma-irradiation in blends of PVP and PVA with plasticizers, being an efficient process for the preparation of hydrogels with simultaneous synthesis of AgNPs. Accordingly, hydrogels with AgNPs have potential for use in infected wounds and burns.

Recovering/recycling of butyl and halobutyl rubbers compounds by ionizing radiation

Polymeric materials (plastics and rubbers) attain a continuously and increasing proportion of litter discarded in landfills; their impact in environment are more and more concerning. The implementation of new technologies toward polymeric residues reduction, acceptable under environmental viewpoint and at an effective cost, proved to be a great problem, due to inhering complexities for polymers re-use. Ionizing radiation is capable to change structure and properties of polymeric materials; it is an expectation for problem solving of polymeric residues management.

Butyl and halobutyl rubbers are used in a comprehensive scale, in a great variety of applications such as tires spare-parts and various artifacts. Rubbers are provided with a very low natural decomposition, due to their chemical structure weather resistant and to enzymatic degradation and microorganisms. Rubber recovering is difficult by its insolubility due to very crosslinked structures. Besides, this tridimensional structure shows a lot of problems for material recovering and reprocessing.

So, the most of rubber residues, especially tires, are discarded and disposed in landfills. In other situations, they are used as combustible and incinerated to produce power; besides, the cost of these operations is very high. Other forms of reuse of rubber include: use in asphalt, manufacture of soles for shoes, rubber seals, rainwater pipes, floors for poly-sports courts, industrial floors, and carpets for automobiles. According to this, recycling and recovering are the best options for residues management.

In spite of various processes already developed and applied toward rubber recycling, the viability of these processes presents many challenges, either technical or referring to material quality. The major effect of high energy photon, as gamma rays in butyl and halogenated butyl rubbers is the generation of free radicals, along changes in mechanical properties.

Butyl and halobutyl rubbers, subjected to high energy radiation, are able to occur in a variety of chemical reactions following initial ionizations and exciting events. These reactions change rubber molar mass via scission or crosslinking and affects physical and mechanical properties. The major ionizing radiation effect in butyl rubber is chain-scission accompanied by a significant reduction in molar mass. Radiation energy transference to butyl rubber does not occur selectively, but the low degree on unsaturation in these rubbers implies in a more quickly scission. Nevertheless, halogenated butyl rubbers answer in a different way to high energy radiation effects. Changes in mean molar mass changes too gel content.

The addition of halogen atoms in the butyl rubber promotes a molecular rearrangement on the dehydrohalogenation of halobutyl rubber to form a double bond in secondary and tertiary carbon in bromobutyl and chlorobutyl rubbers, respectively, which facilitates the formation of cross-links when exposed to radiation high energy.
One of the most promising applications of degradation induced by radiation is the recovery of scrap butyl rubber. It was developed a controlled degradation process (de-vulcanization) in butyl and halobutyl rubbers (chlorine and bromine), in order to characterize their availability for changing their properties. The rubber devulcanized induced by high energy degradation was tested for reuse in the original formulation of the mixture of rubber and can replace some parts of the pistine in the manufacture of final products.

Butyl and halobutyl rubbers compounds were subjected to gamma radiation, in air, at 5 kGy, 15 kGy, 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy, in a gamma radiator, ^{60}Co. Mechanical essays of tension and elongation at break showed chain-scission at doses up to 25 kGy; for doses higher than 50 kGy, it was observed an intense degradation. Especially butyl rubber, halogenated rubbers are a little more radiation resistant. Irradiated butyl, bromobutyl and chlorobutyl rubber compounds and sheared at 25 kGy doses presented compatible results between scission and crosslinking and, so, they were selected for the mixtures between pristine and recovered rubber.

The assessment of physical-chemical properties of compounds comprising recovered rubber showed that the addition of recovered rubber via irradiation and shearing favors a slight decreasing in tensile and elongation at break. Nevertheless, results indicate a compatibility of this incorporation. In summary, it was possible to conclude that, in spite of further adjustments in formulations, containing recovering of butyl and halobutyl rubbers, the strategy of a previous irradiation and a further shearing showed a great potential in recycling scenery.

Development of sulfonated multifunctionais fluoroelastomers based on nanocomposites
Polymer nanocomposite is a material formed by a polymer matrix and, usually, an inorganic compound. This inorganic material has nanometers with size of 100nm and is dispersed in the matrix. These nanocomposites have been studying in Universities and industries because of the final properties presented by this kind of material.

The combination of properties of organic and inorganic materials revealed an improvement of mechanical, thermal, electrical and optical properties. In the case of nanocomposites the same behaviour was notice due to the incorporation of inorganic nanoparticles in the polymer chain. In this work the effect of incorporation of inorganic nanoparticle in the fluoroelastomer matrix has been studied. The selection of materials is very important because the mixture process and quality of final product.

The fluoroelastomer has selected as the matrix polymer because of its properties, such as: solubility; chemical resistant to aliphatic and aromatic hydrocarbons; physical resistant to high temperature; low gas permeability; and others. The inorganic nanoparticles are clay and a silsesquioxane polymer (POSS). The objectives of the use of these particles are improving the mechanical property, reducing the swelling of the elastomer and maintaining the dimensional stability. The incorporation was carried out by mixture process in a two roll cylinder at room temperature. After the incorporation the samples were pressed in order to vulcanized and to obtained films with 0,2 mm thickness. The films will be submitted to gamma radiation to induce graft polymerization by simultaneous method. After irradiation the films will be immersed in the sulfonation solution to complete the experimental part.

Development of partially biodegradable foams from PP/HMSPP blends with natural and synthetic polymers
Structural foams have a comprehensive application field, being used in order to improve appearance of insulation structures or to reduce costs involving materials, besides their applications in building and construction markets. Most thermoplastics can be extruded into structural foams; commercial activities have concentrated on the lower cost thermoplastic, such as Polypropylene (PP).

Polypropylene (PP) is a commodity plastic that accounts for more than 70% of total plastics market; since polymeric materials are immune to microbial degrading, they remain in the soil and in landfills as a semi-permanent residue. PP undergoes crosslinking, inducing changes in its properties, enabling its use in various applications, at distinct process conditions - HMSPP. So, enormous production and use of polymers, in general, lead to their accumulation in the environment; as they are not easily degraded by microorganisms, they present a serious source of pollution affecting both flora and fauna. These polymers are very bio-resistant due to the involvement of only carbon atoms in main chain with no hydrolysable functional group. Non-degradable plastics accumulate in the environment at a rate of 25 million tons per year.

Polymeric discard of PP and its derivatives/ameliorations, as well structural foams from them is, admittedly, one of the most challenging classes of waste to dispose of, in such a degree that their discarding is being blamed for shortening the life span of a sanitary landfill. Several possibilities have been considered to minimize the environmental impact caused by the use of conventional polymers. Polymeric materials can undergo physical, chemical, and biological degradation or combination of all these due to the presence of moisture, air, temperature, light (photo-degradation), high energy radiation (UV, gamma radiation) or microorganisms (bacteria or fungi). Efforts have been made to enhance the rate of biodegradation of these recalcitrant polymers by modifying them or initiating the degradation process by generating free radicals etc. The rate of the biodegradation can be enhanced by blending them with biodegradable natural and synthetic polymers. The presence of any biodegradable polymer as a blend will affect the behavior of the polyolefins and will act as an initiator for their oxidative degradation by heat, light, ionizing radiation and microbes.

Sugarcane bagasse used as natural polymer showed a slight biodegradability, even at 10% in natural basis 50% PP/HMSPP foam, independent of particle size: 150 and 355 µm. Compounds at 15, 30 and 50% showed a good miscibility with natural basis besides an effective biodegradability. PHB and PLA, both synthetic polymers used at 10, 15, 30 and 50%, in natural 50% PP/HMSPP basis did not show an effective biodegradability behavior when compared to sugarcane bagasse; changes in their structure are being presently assessed by *Laboratory Soil Burial*, *EIV*, *DSC*, *TGA*. All compositions were previously subjected to oven test, 120º C, for a 96h-period, before burial test, and did not show any change after unburying; 200ºC showed to be detrimental for all samples and 160ºC samples are being in evaluation.

200 kGy and 500 kGy gamma doses applied in samples comprising 10% of sugarcane bagasse, PLA and PHB imparted wrinkles on surface, after burying, that caused water uptake, acting as a trigger for degradation process, by inlet of soil microorganisms. Thermal behavior for all samples showed crystallinity and melting point results within expectations and related to complete miscibility among materials involved. Mechanical essays accomplished in 50% PP/HMSPP foams, at 10, 15, 30 and 50% of sugarcane bagasse proved the efficacy of reinforcement of these fibers, besides their contribution to minimize environmental pollution.

Analytical Chemistry

Quality system based on ABNT ISO/IEC 17025 Norm
In order to align to the requirements of Nuclear Fuel Cycle, a Quality System based on the ABNT ISO/IEC 17025 norm is being implemented in the analytical laboratories. As required, laws and rules compliances, personnel training, documentation, processes and environment monitoring and controlling are examples of what issues are to be done. Existing analytical procedures are being configured and new ones are in course according to that norm. As the system will be implemented, many benefits are expected not only about organization, but also in the quality of results. Procedure validation and the estimative of measurement uncertainties allowed increasing the

knowledge of what is being done. In a broader view, this local system is part of the institutional integrated quality system management policy which includes other norms of conformity, such as the ABNT NBR ISO 9001. As the system is implemented, higher levels of standards are met showing the way for total conformity assessment.

Analytical chemistry for environmental diagnosis
The Laboratories of Chemistry and Environmental Diagnosis Center - CQMA, have established methodologies for evaluation of physical-chemical, chemical and toxicological parameters to support several research projects in development for environmental diagnosis.
All methodologies adopted are established in the standard methods (ASTM, EPA) or specified by the clients. The classic methods and instrumental techniques analysis such as atomic absorption spectrometry (AAS), inductively coupled plasma emission spectrometry (ICP-OES), ion chromatography (IC), gas chromatography (GC), gas chromatography mass spectrometry (GCMS), high performance liquid chromatography (HPLC;), X-ray fluorescence (WD-XRFS), differential pulse anodic stripping voltammetry (DP-ASV) have been used.

The Center has been participating in several international interlaboratory programs sponsored by: CETAMA (Etablissement Comission des Analyse Méthods, France), IAEA (International Atomic Energy Agency), INTI (Instituto Nacional de Tecnologia Industrial, Argentina), SENAC (Brasil), ABACC (The Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials), SABESP (Basic Sanitation Company of the State of São Paulo, Brasil) and Rede Metrológica Rio Grande do Sul (Brasil). The Quality Handbook according to ISO GUIDE 17025 has been elaborated. The Laboratory of Chemical and Isotopic Characterization - LCQ has been accorded the prestigious INMETRO Certificate of Accreditation in accordance with ISO/IEO 17025:2005. Several methodologies were established to support research projects in development:

Environmental
- The specificity and sensitivity in the pesticides analyses were enhanced by a new methodology using solid-phase extraction followed by high performance liquid and gas chromatography mass spectrometry (GCMS). The impact of pesticides use in agriculture was verified.
- Metal evaluation in top water and drinking water.
- Metal evaluation for industry wastewater.
- Metal evaluation in sediments and soils.

IEA-R1 Reactor
- Evaluation of IEA-R1 water quality.

Brazilian ion chomatograpy proficiency test - A five year evaluation
This work will discuss the results obtained in the analysis of the 6 most common anions in water, during the last five years of the Ion Chromatography Proficiency Testing (PT) Program. PT's were provided by Rede Metrológica do Rio Grande do Sul - RMRS that is one of the most active metrological groups in Latin America. Since 2007 RMRS has launched a yearly PT, sponsored by two main Ion Chromatography (IC) manufacturer companies, acting in Brazil. The participant's performance is done by the most usual approach, by using Z-score and the program follows the procedures listed at ISO/IEC 17043, at ILAC-G13:08, and ISO/DIS13528. The technical support to prepare, store and to perform the stability and homogeneity tests came from the water supply company of the Rio Grande do Sul, CORSAN. The IC aspects observed in the PT were more recently evaluated by IPEN-CNEN/SP, one of the first laboratories to use this technique in Brazil, with almost 30 years of experience on IC.

Development and validation of analytical methodology for determination of pharmaceutical compounds in surface and surface treated water samples by ultra performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS)
The relevant concept of sustainability of the present day leads people to think about the treatment of natural resources and particularly in the quanlity and scarcity of water. The serious problems regarding the management of municipal waste in the country, from production, collection and disposal are the challenges facing municipalities and society in general. The increasing use of pharmaceutical drugs most abundant generates a demand for waste that eventually reach the river beds. With advancement of technologies and know you can monitor the waste that directly and indirectly affect the waters of river basins.

The objective of this study was to develop and validade analytical methods for residues of drugs (aspirin, sodium diclofenac, paracetamol, ibuprofen and fenoprofen) in water using ultra performance liquida chromatography coupled to tandem mass spectrometry (UPLC-MS/MS). We used two different mobile phases. For the drugs paracetamol and diclofenac was used as mobile phase water:methanol (1:1, v/v) with addition of formic acid in positive electrospray ionization mode. For drugs acetyl salicylic acid, ibuprofen and fenoprofen was used mobile phase water:methanol (1:1, v/v) with addition of ammonium acetate and negative electrospray ionization mode. The performance of the method was evaluated on the following parameters: specificity and selectivity, working range, lineariry, limit of detection and limit of quantification, accuracy, ruggedness and uncertainty measurement. The result obtained proved the suitability of the method for fit purpose. The values obtained for the decision limit (ccα) and detection capability (ccβ) were 0.21 and 0.34 $\mu g\ L^{-1}$, diclofenac 2.42 and 3.24 μgL^{-1}, ASA 1.56 and 2.45 μgL^{-1}, respectively.

The methodology was applied in the characterization of samples of surface water (raw) and treated from catchment areas and water treatment basin of Paraíba do Sul were two distinct collections, September/2011 and November 2010 in the municipalities of Guararema, São José dos Campos, Taubaté and Pindamonhangaba. In 32,2% of all samples, five samples of 16 raw water samples, residues were found for paracetamol. The results were presented in a concentration range from 0.10 to 0.50 $\mu g\ L^{-1}$.

Determination of plasticizer in drinking water using gas chromatography and mass spectrometry
This study investigated the levels of plasticizer endocrine disruptores (diethyl phthalate, dibuthyl phthalate, and bisphenol A) in drinking water at Paraíba do Sul River (SP-Brazil) region and release compounds from bottled water. An analyytical method employing solid fase extraction and CG/MS was optimized and validated. The results showed that the melhod is selective, linear (r^2> 0.99), precise (RSD < 12 %), accurate (recoveries between 62 and 105%), senditive and robust. Applying the method, the presence of all studied pollutants in dinking water was observed for the three sampled plasticizers. These plasticizers were not found in mineral bottled water, before or after storage.

X- ray fluorescence techniques applied to environmental, geological and biological studies

Chemical characterization of nuclear and non-nuclear materials

R&D activities
The X-Ray Fluorescence Laboratory (LFX) has worked in environmental, biological and nuclear areas, establishing new analytical methodologies using the X-ray fluorescence spectrometries (WDXRF, EDXRF and PXRF systems). Different matrices, such as soils, sediments, lubricating oils, treated wood, metal environmental pollution monitoring trees, organic fluids and nuclear and non-nuclear materials have been analyzed. The R&D activities have been supported by CNPq, FINEP and IAEA research financial organisms. The main projects, carried out and ongoing, are listed below.

Environmental area
Environmental diagnostic: The coal power plant produces bottom and fly ashes during the combustion. The treatment and disposal residues of ashes are important topics for evaluation of soil and ground water contamination. The total inorganic elements (Na, Mg, Al, Si, Ca, Ti, Fe, P, S, V, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr, Zr, Ba and Pb) in soil,

ashes, coals and grasses were determined at Figueira coal power plant, located in Paraná, Brazil.

Metal pollution: Brazil stands out in successful biofuel technology in the automotive full flex type. Currently, full flex type cars, (83% of demand), amount to about 3 mi vehicles. The determination of wear metals in used lubricating oils is an important factor for preventative maintenance and motor engineering performance, in the automobile area, and for the concern about public health and environmental pollution. Wear metals have been determined in the used lubricating oils collected from biofuel vehicles, full flex type, to evaluate environmental impact in metal release. The project has been performed with GM (General Motors) cooperation.

Wood preservation: Brazil produces around 1,2 mi m^3 of treated wood to meet the annual demand of railways, electric, rural and construction sectors. The treated wood should be according to Brazilian norms; the most wood preservative product used in Brazil is CCA (chromated copper arsenate). The analytical methodologies using the EDXRF (Energy dispersive X-ray Fluorescence Spectrometry) and PXRF (Portable X-ray Fluorescence Spectrometry) have been performed to Cu, Cr and As determination, in treated eucalyptus (*Eucaliptus ssp*) woods. The results will be compared with FAAS and NAA data. This study has been carried out in a joint work with IPT (Instituto de Pesquisas Tecnológicas, SP).

Clinical and biological area
Elements such as Na, Mg, P, Cl, S, K Ca and Fe in the whole blood of humans (healthy population) and laboratory animals (Dmd^{mdx}/J mice, Crioula breed horse, golden hamster) were analyzed for reference interval values determination.

Chemical characterization of biological materials, such as rabbit urinary stone, lung tissues and saliva from *Amblyomma Cajannense* specie, has been outlined for clinical studies. Electrolytic elements, such as Ca, Cl, K, Mg, Na, S, Fe and Zn are important for athletes submitted to constant and hard physical efforts, because their health and physical performance depend on the variation and concentration of these electrolytic elements. The analytical methodology for the determination of the electrolytic elements, in whole blood samples, has been established by EDXRF (Energy dispersive X-ray Fluorescence Spectrometry) for the long distance runner; and the results will be compared with NAA (Neutron Activation Analysis) data.

Nuclear area
Nuclear fuel: The chemical characterization of the nuclear fuel U_3Si_2 used in the IEA-R1 reactor has been performed by WDXRF spectrometry. U_{total} and Si content plus impurities, such as B, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sn and Pb have been determined using the Multivariate Calibration method.

Nuclear related materials: In the fabrication of nuclear reactor core parts, Zircaloys machining scrapes are generated. Two metallurgical processes (VAR furnace and powder metallurgy) were applied to the evaluation of the scrap recycling process, at the CCTM (Centro de Ciência e Tecnologia de Materiais, IPEN). The characterization of the major constituents (Cr, Fe, Sn and Hf) and impurities, such as Al, Ca, Cu, Mg, Ni, Mn, Nb, Pb, Si, Ti, V and W, was determined by EDXRF spectrometry.

Others
The FCC process (Fluid Catalytic Cracking) of catalysis is important to modern manufacturing industries. The catalysts regeneration by gamma ray irradiation has been studied in CTR (Centro de Tecnologia das Radiações)/IPEN. The chemical characterization (Al, Si, La, Fe, Mo, S, K, P and metal impurities) of loaded and unloaded catalysts has been performed to evaluate the gamma ray irradiation process.

The desulfurization process in petroleum and diesel fuel has been studied by electron beam processing in CTR/IPEN. Sulphur withdrawal degree in different organic solvents has been performed by EDXRF spectrometry. The chemical characterization of Brazilian medicinal herbals, such as *Campomanesia xanthocarpa Berg* and metal environmental pollution monitoring trees have been analyzed by EDXR spectrometry, for medical and environmental studies.

X-ray fluorescence undergraduate, graduate and short extension courses
The X-ray fluorescence laboratory offers an undergraduate (IPN 0014:X-ray fluorescence spectrometry) at USP (University of São Paulo) and a graduate course (TNM 5813:X-ray fluorescence spectrometries, theory and application) in Nuclear Technology program in association with the University of São Paulo, USP. Also, X-ray fluorescence short training extension courses have been offered for researchers and technicians of Brazilian and Latin American universities and industries.

Quality assurance
In the period, the LFX has continued the ISO IEC 17025:2005 norm establishment. Several topics of the Quality Manual were improved and adapted according to new requirements. The annual internal audit has been carried out by SGI/IPEN. The laboratory has participated in national Inter-comparison program (PEP-FINEP, Brazil) and international X-ray Proficiency Testing for X-ray Laboratory programs (PFXRFIAEA09, PTXRFIAEA10), organized by the IAEA (International Atomic Energy Agency).

Nuclear forensic program

Since nuclear energy was first utilized, the risk related with criminal or unauthorized acts involving nuclear or other radioactive (RN) materials have been a serious concern for the entire global nuclear community. During the last decades, the possibility that terrorists or other criminals might obtain RN materials for malicious use has become a real threat to global security especially after the collapse of the Soviet Union, at the end of the 1980's, when several tons of these materials were stolen. This concern was enhanced in the early years of the 1990's when several attempts of illicit trafficking of these materials were identified.

The inclusion of nuclear materials into classical forensic investigations led the definition of a new science called "nuclear forensic science". Nuclear forensic science is a branch of criminology that deals with crimes involving nuclear or other radioactive materials. The main objective of this new science is the identification of the nature and origin of the seized material, and of any intent to use it, and requires collaborating efforts of different technical and scientific expertise.

The nuclear forensic program at IPEN, started 2007 by means of a research contract with the International Atomic Energy Agency. The first achievement of the project was the creation of the Brazilian Network of Laboratories on Nuclear Forensic Science (BNLNFS) using the scientific expertise of Brazilian National Commission of Nuclear Energy (CNEN) nuclear scientists and the existing infrastructure. The BNLNFS partners six laboratories located at Nuclear and Energy Research Institute (IPEN), and The Laboratory of Poços de Caldas - CNEN - Rio de Janeiro, and has the support of São Paulo State Police and Federal Police, Brasília. The associated laboratories implemented techniques recommended by the IAEA to conduct an examination consistent with nuclear forensics model action plan.

Since its establishment the BNFL has participated in several international exercises and conducted the first national exercise simulating a real situation where unknown samples were seized, its chemical, physical, morphological and isotopic characterization established and at the end, its origin evaluated.

Chemical metrology

Nowadays, there is no doubt concerning the importance of chemical measurements in modern society, influencing different aspects of the quality of life of the human beings. So, once every year many millions of chemical measurements are made in different parts of the world and for a wide variety of purposes its important to establish general criteria to be followed not only for the ones which perform these analysis as well as the others that have to understand and interpret the results. In

this scenarios, some decades ago, a new branch of science was created: Chemical Metrology (CM). CM is one branch of Metrology and defined as the science of chemical measurements.

The CM activities at our laboratory started during the 1990's with a quality control program and the establishment of the main analytical procedures recommended by international organizations with the objective to guarantee the quality and traceability of the analytical results. As a consequence, the laboratory was accredited by the Brazilian National Institute of Metrology, Quality and Technology (INMETRO) for measurements of mercury in fish tissues. During the last decade the laboratory started a program with the objective to develop certified reference materials (CRM) following the International Organization for Standardization (ISO) protocols.

The first material produced was Dourada 1, a fish tissue certified in the following constituents: As, Pb, Cd, Hg and Met-Hg. It was the first CRM produced in Brazil for fish tissues with the innovation of using the isotopic dilution technique to certify Hg and Met-Hg. Continuing the program, new materials were developed but, this time, to be used for proficiency tests (PT). The PT are largely used to evaluated the analytical capacity of the laboratories being an important part of the accreditation process. The selected program was metals in fish tissue once in Brazil there is no providers for such program and the relevance of fisheries in the Brazilian balance of trade. Two materials were prepared and certified also following the ISO recommendations. The material were send to ten national laboratories including all laboratories belonging to the Ministry of Agriculture, livestock and supply network. It is important to notice that this PT was the first one completely developed in Brazil and based on the results a more comprehensive program is in progress now involving private laboratories as well as fish producers.

The mankind has faced challenges from energy needs and prices, resource shortages and global environmental problems. Therefore, there are new needs such as knowledge-based products or services that improve operational performance, productivity, or efficiency while reducing costs, inputs, energy consumption, waste or pollution. Nowadays, products, services or processes should use limited or zero non-renewable resources and creates significantly less waste. Such technologies are named Clean Technologies that use energy, water and raw materials more efficiently, create less waste or toxicity, deliver equal or superior performance, and promote cost reduction and/or increased revenues. Given the environmental benefits these technologies confer, clean technology is an intrinsic part of a sustainable economy. Some major clean technology sectors are energy, water, manufacturing, advanced materials and transportation. The pollution control and waste reduction are also some important fields, consequence of the public perception of problems like global warming and the impact from the burning of fossil fuels, besides the introduction of contaminants into the environment, as a result of industrial activities. Clean technologies are seen to be the next engine of economic growth and the IPEN has dedicated attention and research initiatives in accordance with this approach.

Complete degradation of BHC and other pesticides by molten salt oxidation

In the last decades, there were significant changes in the perception by the public of the necessity of environmental preservation. Pesticides banned, obsolete or discarded constitute a serious environmental risk around the world, especially in developing countries. Pesticides are among the compounds that constitute the group of so-called POPs, or persistent organic pollutants that are regulated internationally by the Basel Convention. Among the major POPs could be cited pesticides, dioxins and PCBs that represent, according to the United Nations Industrial Development Organization - UNIDO, one of the most serious and urgent problems to be faced, because on the one hand, its wide dissemination in environment and, secondly, because of its properties and characteristics, which determine its persistence in soil and water. The United Nations Environmental Protection - UNEP, for example, launched a global action for the reduction and/or elimination of emissions and discharges of 12 specific POPs, also known as “dirty dozen” (Aldrin, Chlordane, Mirex, Dieldrin, DDT, Dioxins, Furans, PCBs, Endrin, Heptachlor, Toxaphene and BHC), besides the adoption of scientific criteria for the possible inclusion of others. Particularly, the HCHS, or Hexachlorcyclohexanes also called BHC or Lindane, are organochloride insecticides that have been banned in most countries in the 70s and 80s years.

As the disposition of hazardous wastes, in sanitary landfills and through incineration, has become a problem gradually more complex, because the decrease of the available space for storage or the increase of the demands of the governmental regulations. One of the predominant concepts currently is that the wastes should be destroyed in some point of their cycle of use, specially the dangerous ones, in reason of the risk that they represent for human beings, animals and plants. The worldwide interest in the development of advanced decomposition technologies of wastes elapses, mainly, of the problems created by the denominated POPs - persistent organic pollutants.
The thermal decomposition has been commercially used in the disposal of hazardous wastes, mainly the incineration, whose most important characteristic is the combustion with flame. However, the incineration technologies have failed to meet some performance criteria. Incinerators can release by the chimneys hazardous compounds, among which could be mentioned: heavy metals, organic material partially burned as polyvinyl chloride (PVC) or other products resulting of the incomplete combustion (PCIs), polycyclic aromatic hydrocarbons (PAHs).

Molten salt oxidation of wastes

An alternative to the incineration, for the treatment of a vast range of dangerous residues or no, it is the decomposition through the submerged oxidation in molten salt baths. The molten salt oxidation was developed in the fifties by the Rockwell International Co. for U.S. Atomic Energy Commission using molten fluorides. Initially, it was developed for activities of the nuclear fuel cycle not related to the wastes. Differently of the incineration, the process doesn’t request a flame to begin or to continue the reaction. The molten salt oxidation - MSO - consists of a submerged thermal decomposition of organic materials. It allows the immediately oxidation of the hydrocarbons molecules to carbon dioxide and water in the steam form. The technique could be described, in a simpler manner, as a simultaneous process of oxidation and scrubbing of the reaction products. This can be obtained by the injection of the material to be burned and air in excess below the surface of a melted salt, or melted salt mixtures as, for instance, sodium carbonate and sodium sulfate, maintained in temperatures in the range from 900°C to 1000°C. The salts are not consumed in the process, except in the case of decomposition of wastes containing halogens atoms, like chlorides, for instance. In this case, it is formed sodium chloride by the reaction of the chlorine and the sodium of the salt. This is an intrinsically important characteristic of the molten salt oxidation, since the dioxin and furans formation is avoided by the mentioned reaction. The gases introduced or generated in the process are forced through the saline bath before leaving the equipment, what provides a wash action. Among several advantages, such as oxidative reactions that transform completely the components of the organic waste in just CO_2 and water, the process equipment can be built in small scale.

Development of pesticides decomposition by molten salt oxidation at IPEN-CNEN/SP

The study involved the design and construction of equipment for organochloride waste decomposition tests at IPEN. Built equipment has dimensions that could be classified as pilot scale, and aims to demonstrate the applicability of the method in the decomposition of pesticides and to obtain parameters for the future construction of a larger unit.

As shown in the Figure 9, the equipment is constituted by two reactor vessels and respective individual electric heating systems. The tandem assembling is to permit introduce the off gases from the first reactor in the second one, as presented in the Figure 10. This assembling permits to collect samples of the decomposition products of both reactors as well as the use of different salt mixtures and/or molten salt temperatures in each reactor.

Figure 9. Pictures of the molten salt equipment developed at IPEN.

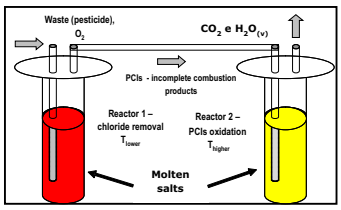

Figure 10. Schematic drawing of the molten salt oxidation of pesticides.

As a complementary activity, it was also necessary to choose a study of salt mixtures, especially in terms of reducing the melting temperature, and compatibility of pre-selected salt mixtures with the material of the reactor vessel. As the use of pure sodium carbonate prevent the realization of the process below the melting temperature of 851°C, in this work we investigated eutectic mixtures of sodium hydroxide and sodium carbonate, whose melting temperature is 286°C (41% sodium carbonate and 59% sodium hydroxide - mass percentages) and mixtures of Li_2CO_3-Na_2CO_3-K_2CO_3, whose eutectic composition is 32,2% A - 42,7% B - 25,8% (percentages in mass) and melting temperature of 397°C, for conducting studies of degradation of the

pesticide BHC - hexachlorocyclohexane at different temperatures in the range 300-900°C. It was chosen a mixture of carbonates of Li, Na and K with composition of 20A-60B-20C (mass ratio) respectively to decrease the melting temperature as much as possible, since lithium carbonate is relatively expensive. The waste (BHC in powder) was introduced with air in the first reactor and the gaseous products of the decomposition reactions were introduced in the second reactor. Gas samples after the first reactor and after the second reactor were collected in each decomposition experiment, using gas chromatographic syringe and analyzed by gas chromatography and mass spectrometry coupled with gas chromatography.

The results have proved that chlorine can be retained at low temperatures, as mentioned above, by forming the corresponding chlorine salts, i.e. lithium, sodium and potassium chloride. These innocuous chlorides salts are retained in the molten salt bath. Even the not decomposed BHC or its molecular fragments could be avoided by using a higher molten salt column or by the reduction of introduction rate.

Hydrogenation of oil by using microwave radiation

Several types of petroleum hydrotreating process can benefit from microwave technique. It has recently been studied all over the world to indentify (qualitatively and quantitatively) and define the mechanism of microwave-material interaction. The application of this process in our country is a very recent field and has been studied as a new tool in materials processing for heavy oil degradation, which uses high temperature for desulfurization of oil and diesel. The knowledge of this technology is important to begin the development process in industrial scale and consequently in reducing the environmental pollution caused by residues (such as sulphur and nitrogen). Microwaves are a form of electromagnetic energy in the frequency band from 300MHz to 300GHz (not ionizing radiation). Industrial microwave processing is usually accomplished at a frequency of a 2,45GHz (which corresponds to a wavelength of 12,24 cm) to avoid interference with telecommunication and cellular phone frequencies.

Microwave processing offers numerous advantages in relation to conventional heating methods (convection or conduction), where the material surface heats first and then the heat moves inward. One of the most important characteristics is saving energy, because the material absorbs microwaves readily (the heat is generated from the inner parts to the surface of the material) reducing the processing time. Also the selective energy absorption allows heating in specific points of the material. This process is environmentally clean because it reduces pollutant emissions. Finally, the microwave heating requires no appreciable amount of time to effect temperature changes such as conventional methods and when the microwave device is turned off the effect of these electromagnetic waves are instantaneously stopped. A reaction system microwave-assisted (with power until 2kW continuous or 8kW pulsed) and conventional heating for processing of hydrocarbons mixtures has been used at IPEN-CNEN/SP to decrease naphthenic acidity, the content of sulphur (HDS-hydrodesulphurization) of nitrogen (HDN-hydrodenitrilation). It operates in batch mode at high temperatures (until 500°C) and pressures of hydrogen (until 20MPa) - Fig. 11.

Figure 11. Batch reaction system microwave-assisted and conventional heating.

Another similar reaction system was developed and it is able to operate in continuous flow mode at high temperatures and pressures. Preliminary studies will be made for use in the same mixtures (Fig. 12). These apparatus are connected to an electronic control and supervision unit which enables interaction with, and measurement and monitoring of, the variables involved in the process. A Programmable Logic Controller (PLC) digitalizes and processes the signal for the microwave radiation (transmitted and reflected) identified by the wave sensors by means of a computer program. Project developed in collaboration with CENPES-PETROBRAS.

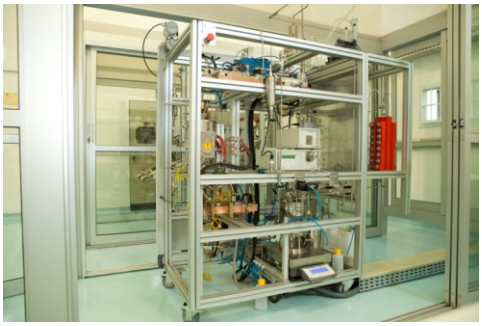

Figure 12. Reaction system of continuous flow microwave-assisted and conventional heating.

Study of biomass and magnetite nanoparticles in the preparation of magnetic adsorbents of metals and dyes for wastewater treatment

Biomass is a natural polymer which is composed of various types of polysaccharides. Some biomass species have active sites capable of binding with metal ions and organic molecules in aqueous medium by chemisorption or physisorption and have been investigated as adsorbents of contaminants in the process of wastewater treatment. These biomass species are called biosorbents. The activities of aquaculture and agro-industries generate a significant quantity of residual biomass, as byproduct, that can become an important source of production of new low-cost biosorbents. The use of residual biomass as adsorbents is an alternative of sustainable technology for wastewater treatment.

Another class of adsorbents that have been extensively studied are magnetite nanoparticles, an iron oxide, which besides their adsorptive properties are also magnetic, so are naturally magnetic adsorbents. A magnetic adsorbent has a great advantage over the non-magnetic adsorbents in a treatment process of contaminated aqueous medium. After adsorption of the contaminants on the magnetic adsorbent, this can be removed from the liquid medium by magnetic separation technique. This technique simplifies the slid-liquid separation in the wastewater treatment process, and also, eliminates the generation of secondary waste and can be considered a clean technology.

The incorporation of nanoparticles of magnetite in non-magnetic sorbents leads to obtaining of a new magnetic adsorbent that has adsorptive characteristics enhanced and magnetic properties. The highlight of this research is to prepare adsorbents from the manipulation of a residual biomass adsorbent with synthesized magnetite nanoparticles for the development of a clean technology by application of techniques of adsorption and magnetic separation for the processing of radioactive effluents and wastewater as well as for environmental remediation.

In period 2011-2013, the sugarcane bagasse, coir, banana peel, corn husk, scales of Corvina fish were washed, dried, ground, sieved between 30 and 100 mesh for obtaining biosorbents. Flakes of chitin and chitosan, derived from the exoskeleton of crustaceans, were purchased and used directly for adsorption studies. Removal of Mo ions was investigated from nitric and alkaline solutions. All assays were performed in batch and the solid-liquid separation was conducted by filtration.

Influence of pH, kinetics, isotherms, models of pseudo-first order, pseudo-second order, Langmuir and Freundlich were studied. Results indicated that the acidity of the solution favored the Mo adsorption on the biosorbents. Adsorption values higher than 85% were found at pH 2.0 for sugarcane bagasse, coir, corn husk, chitin and chitosan. From the alkaline solutions, the adsorption values were lower than 45%. Among biosorbents the coir showed better adsorption capacity for Mo in a wider range of pH as shown in Fig. 13. This work showed that the biomass has high potential to be used as biosorbent of molybdenum ions from acidic wastewater, and the kinetics suggested high-affinity adsorption governed by pseudo-second order sorption.

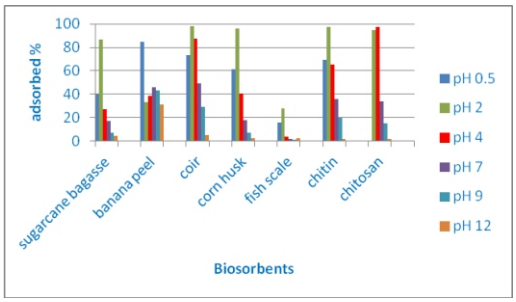

Figure 13. Effect of pH on the molybdenum adsorption on the biosorbents. [Mo] = 0.5 mg L^{-1}.

The scales of Corvina fish were also investigated for U removal from nitric solution. The adsorption of U ions at pH 4 was higher than 80% in contrast to the value found for the Mo ions that was less than 5%. The preliminary results are very promising, showing great perspectives of application of the scales of Corvina fish as biosorbent for uranyl ions in radioactive wastewater treatment process.

Synthesized magnetite nanoparticles were incorporated into the particulates of sugarcane bagasse and chitosan flakes to obtain the magnetic adsorbents. These exhibited a magnetic response of intense attraction in the presence of a magnetic field without becoming permanently magnetized. Adsorption potential for the ions of U was studied and the feasibility of application of the technique of magnetic separation was verified. The results demonstrated that they are effective on the adsorption for UO_2^{2+} ions. The removal was from 90% to 99%, the adsorption capacity of the magnetic adsorbent was higher than of the magnetite nanoparticles and allowed the solid-liquid separation using a magnet. Also the desorption behavior using carbonate and oxalate ions was investigated for magnetic adsorbent of chitosan. It was recovered 94% of U with carbonate ion under the conditions studied. The chitosan, available as a byproduct of marine food processing, is environmentally safe and can be a low cost adsorbent for U removal from wastewater. The magnetic adsorbent of chitosan is an economically feasible alternative and presents good perspectives of application as a sustainable processing technology for uranium liquid waste treatment.

Another category of residual material studied was coal fly ash, a waste in large volumes from the coal-fired electric power plant. By a controlled alkaline digestion method, coal ash can be converted into zeolite, an effective adsorbent for metal ions and dyes. However, the synthesized zeolite is formed of very fine particles that hinder the processes of filtration and centrifugation. In this period, a magnetic adsorbent of zeolite was prepared from synthesized zeolite combined with magnetite nanoparticles and was characterized by the FTIR, SEM, XRD, TGA and magnetization curves.

This magnetic adsorbent from the coal ash exhibited magnetic properties being easily attracted and separated from the aqueous solutions using a magnet. The performance of magnetic separation technique was evaluated (Fig. 14), and it was comparable to the centrifugation process. The preliminary results showed that the Reactive Orange 16 dye was adsorbed on the magnetic adsorbent indicating a potential application as an alternative and sustainable processing technology for wastewater treatment. The research on magnetic adsorbents produced two patent deposits PI 1102348-1 and PI 1106517-6 in 2011, and one patent letter PI 0302329-0 in 2012.

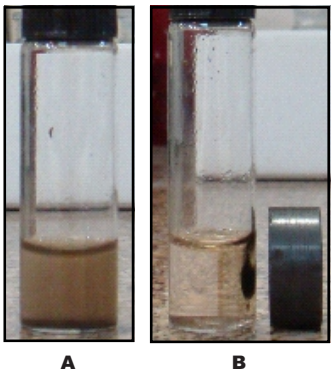

Figure 14. Application of magnetic separation technique: (A) Vial with a suspension of magnetic adsorbent of zeolite in the solution of dye Reactive Orange 16, and (B) same vial where all magnetic adsorbent of zeolite was attracted by a magnet in 5s.

Low-cost adsorbent: Synthesis, characterization and environmental application

Brazilian coals are richer in ash (content of 20-50 wt.%) and poorer in carbon when compared to worldwide coal and coal ash disposal is a serious environmental concern. Only 30% of fly ash is applied as raw material for cement and concrete production. The remaining solid wastes are disposed in on-site ponds, nearby abandoned or active mine sites, or landfills. Reuse of coal ash may provide a new source of revenue for coal-fired power plants and may offset expenses associated with its disposal. In the environmental aspect, the increased use of coal ash can reduce energy consumption, reduce the need for additional landfill space, and conserve natural resources.

In our group we have been developing zeolites synthesized from Brazilian coal fly ash by conventionally hydrothermal treatment and fusion method. Pure zeolites X and A, zeolite from fly ash-iron oxide magnetic nanocomposites, surfactant-modified zeolites and zeolitic materials were synthesized and characterized. In addition, the zeolites from Brazilian coal ash were used as low-cost adsorbents and have proven to be promising materials for the removal of dyes and toxic metals from aqueous solution. Moreover, a considerable reduction in the elements contents and in the toxicity to living organisms (*D. similis* and *V. Ficheri*) was attained in the fly ash zeolitization. Brazilian fly ashes have been also applied as a by-product aggregate in the manufacture of ecological bricks (Figure 15).

Figure 15. Sludge from water treatment plant-coal fly ash-soil-cement bricks.

Other line of research has been developed focusing the conversion of sugarcane straw ash, an agricultural waste of sugar industry with disposal problems, into zeolitic material. Brazil is the largest producer of sugarcane of the world generating 400 million tons per year, on average. An amount of 1 ton of sugarcane generates 270 kg bagasse and 144 kg trash/straw. Zeolitic material was synthesized from sugarcane straw ash by conventional hydrothermal treatment and fusion method. The studies revealed that the zeolitic material was successfully developed from the low cost sugarcane straw ash in the absence of organic templates and without addition of aluminum solution.

Adsorbent studies based on ceramics applied to environmental monitoring and pharmaceutical removal treatment

The development of ceramic adsorbent material as magnetite, diatomite and water treatment plant sludge (WTP sludge) to monitor, adsorb and remove the antibiotic amoxicillin and phosphate from industrial wastewater and domestic sewage. The ceramic material has many desirable properties for environmental use as chemical stability, high surface area, low toxicity and specially for magnetite, the magnetic response. Such material has promoted a low cost wastewater treatment before water discharge on rivers, lakes and reservoirs of São Paulo Metropolitan Area. Nowadays the antibiotics water contamination is considered responsible for the increasing bacterial resistance. Domestic sewage discharges are the main sources and the most responsible contamination for pharmaceutical and endocrine disrupters' in water courses, Figure 16.

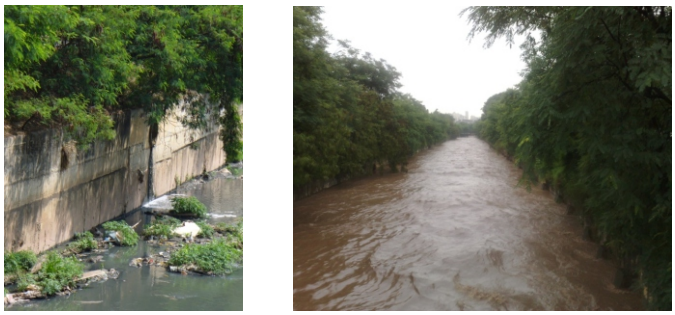

Figure 16. Sewage, garbage discharge and the flooding occurrence at Pirajuçara River - Metropolitan Area of São Paulo.

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Honor Mention and Awards

The project entitled “Attainment of copolymers based on grafting of polymeric matrices” was awarded with the Prize Inventor 2012 PETROBRAS. The research was developed by MSc. Heloisa Augusto Zen and guided by the researcher Dr. Ademar Benévolo Lugão.

The project of master’s degree of Mauro Valério da Silva entitled “Development of bricks with incorporation of coal ash and sludge from water treatment plant” was awarded with the Prize Enfil “Innovation in Environmental Technology”. The work was guided by the researcher Dr. Denise Alves Fungaro. The award's ceremony was held on June 04, 2013 in São Paulo.

The study “Removal of colour and reduction of toxicity in reactive dyes using zeolites from coal fly ash” presented at the Congress SETAC Australasia - Melbourne 2013 (1-3 October at the University of Melbourne in Victoria, Australia) was awarded with the Prize “Best student research poster in ecotoxicology”. The work was guided by the researcher Dr. Denise Alves Fungaro and was part of the master’s degree of Patricia Cunico Ferreira.