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ABSTRACT BOOK

"Bridging the Gap between Science and Governance"

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similar value for caffeine and paracetamol at OASIS HLB. Ibuprofen and Naproxen showed good recovery at Oasis HLB, when a 5mg/L EDTA solution was added in the sample. Salicilic acid showed a poor recovery at Oasis HLB (40%

103 Fast sample preparation method for PBDEs, PCBs, and PAHs in human breast milk for analysis by GC-MS/MS

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Persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) are ubiquitous in the environment. Therefore, humans are exposed to these chemicals generating a risk to toxic effects including endocrine disruption (PCBs and PBDEs) and carcinogenicity (PAHs). The aim of the project was to develop and validate an analytical methodology to determine in human breast milk: PCBs (33 congeners), PBDEs (26 congeners), and PAHs (22 compounds) by using a Gas Chromatography couple to Tandem Mass Spectrometry (GC-MS/MS). The sample treatment procedure was bases on a modified version of the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) approach in addition to two cleanup steps, one with KOH in methanol to remove lipids and the other with Solid Phase Extraction (SPE). Homogenized breast milk samples (20 ml) was place into 50 µl of a polypropylene tubes, after the addition of Ethyl Acetate, and spiked with internal standard of ^{13}C-isotope label standard (^{13}C-PBDEs and ^{13}C-PCBs) and deuterated label standard (^{2}H-PAHs), were vortex for 1 min. HPLC grade water was used instead of sample (20 ml) for the blank procedures. Organic phase separation was induced by addition of NaCl (2 g) and $MgSO_4$ (6 g), the samples were vortex for 1 min, and centrifuged (4500 rpm at 5 min). Extracts were transferred to two vials, 1 ml for gravimetric lipid content and the other 15 ml for cleanup. For the cleanup steps, the extracts were treated with KOH in methanol (saponification for 30 min at 60 °C), centrifuged (2500 rpm at 5 min), and the organic phase were extracted with toluene (3 time with 5 ml). Toluene extracts were concentrated under N_2 gentle stream to 2 ml, passed through Solid Phase Extraction (SPE) column packed with Florisil (1 g), Na_2SO_4 (1 g), and eluted with 10 ml of dicloromethane/n-hexane (1:3). Fractions were concentrated under N_2 gentle stream to 100 µl and transfer to a vial containing inserts for analysis on GC-MS/MS, TSQ™ 8000 Evo Triple Quadrupole GC-MS/MS – Thermo Scientific). The matrix-spiked absolute recoveries of the entire analytical procedure: extraction, cleanup, and SPE steps were > 90% in all cases. Validation of the method included limit od detection (< 1 ppb), limit of quantification (< 2ppb), linear range (5 – 500 ppb), and linearity of calibration curve (R > 0.995).

104 Pesticide metabolites in fish by Clean-up application, solid-liquid extraction and GC-MS analysis for human dietary risk at Ceará coast, Brazil

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The risk to human health and environment due to overuse of pesticides has been increasingly recognized, together with the interest in food quality. Fish are an important food source on which the bioaccumulation of pesticides and their metabolites threatens all consumers. This study investigated the occurrence of pesticide metabolites in catfish from the estuaries of Ceará (ECR), Pacoti (EPR) and Jaguaribe (EJR) rivers, Ceará, Brazil, using gas chromatography-mass spectrometry (GC-MS), and calculated Estimated Daily Intake (EDI) and Risk Quotient (RQ) to assess human health risk due these fish consumption by local population. Catfish were collected on April/May 2016 at ECR (n=11), EPR (n=10) and EJR (n=7) by fishermen, under ICMBio license 51308-1. Metabolites analyzed were: Chlorpyrifos methyl (Chlorp-M), S-metolachlor (S-Metola), 1-Hydroxypyrene (1-OHP), Malaoxon (Malaox), 2-Chloro-4,6-diamino-1,3,5-triazine (2-CAAT), Carbofuran phenol (CarbPhenol) and 3-Phenoxybenzoic acid (3-PBA). Muscle samples were lyophilized, homogenized and submitted to solid-liquid extraction and *clean up* processes. Method performance was validated by linearity (R^2: 0.9815 - 0.9957), sensibility, limits of detection (LOD: 0.33 – 35.99 mg mL^{-1}) and quantification (LOQ: 1.10 – 119.95 mg mL^{-1}), precision (0.20 – 13.47 %) and recovery (45.47 – 60 %), and was satisfactory for detection of all compounds except 1-OHP. Only three were detected in catfish: 3-PBA [3.06 ± 3.88 (EJR) - 7.43 ± 3.38 ngg^{-1} (ECR)], CarbPhenol [6.04 ± 0.0 (ECR, EJR) - 6.68 ± 0.9 ngg^{-1} (EPR)] and Malaox [20.67 ± 0.04 (EJR) - 24.29 ± 3.47 ngg^{-1} (ECR)] and didn't differ between estuaries, despite the diversified pollution, and Malaox contents were significantly higher ($p< 0.001$) for the three estuaries. EDI (mg day $people^{-1}$) calculated were 0.002 – 0.004 (3-PBA), 0.003 (CarbPhenol) and 0.010 – 0.012 (Malaox), but RQ, based on the parental compounds values, was low for 3-PBA (0.03 – 0.07) and Malaox (0.03 – 0.04), and high for CarbPhenol (1.49 – 1.65). Results represent an alert to the high possibility of risks to human health due to the use of pesticides in Brazil, mainly Carbofuran. Besides, the specie *Sciades parkeri*,found in ECR and EJR, is currently classified as Vulnerable. Legal actions for protection and management of tropical estuaries must be performed with strict force, since the conservation of these environments is the fundamental way of ensuring species preservation and ecological relationships balance.

105 Photocatalytic degradation of triclosan: toxicity of byproducts on microalgae Kirchneriella lunaris and Scenedesmus acuminatus

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Triclosan (TCS) is an antimicrobial widely used in various consumer healthcare products, soaps, and some plastic formulations. Due to the broad use a small portion of TCS has been found in various environmental matrices such as water and sediments. Several studies have shown that the sunlight irradiation of TCS via direct or indirect photoreactions produce dichlorodibenzo-*p*-dioxins which represented the major degradation products in aquatic environment . Therefore, understanding of potential effects on aquatic organisms is so important. The algal toxicity tests are relatively simple and inexpensive method to evaluate the toxicity of chemicals. In this work the toxicity of TCS under heterogeneous photocatalysis using UV/TiO_2 was assessed by inhibition of cell growth of microalgae *Kirchneriella lunaris and Scenedesmus acuminatus*. The bioassays were conducted in three different groups. The experiment 1 comprised the Conway medium (control), and the experiment 2 carried out in the Conway + TCS, and the test 3 in the Conway + TCS + UV/TiO_2. All tests contained initial inoculum concentration of 20,000 cells/mL in the test tubes and nominal test concentrations of TCS were 0 to 5.0 mg/L. Algae cells were counted daily and the inhibitory concentration could be estimated after 21 days by measuring the direct fluorescence. The results in the experiment 2 showed significant reduction of 53-62% on both microalgae cell growth from 0.5 mg/L whereas 100% exhibited significant inhibition at 1.0 mg/L. In the test 3 after 60 min of UV/TiO_2 irradiation was not found to have significant effects on any of the algae and the average inhibition was 1.75%. These results indicate that the process applied has not generates toxic byproducts to the microalgae *Kirchneriella lunares and Scenedesmus acuminatus*.

106 The expression of uncertainty of measurement in toxicity tests results

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Acute and chronic toxicity testing with effluents carried by Aquatic Ecotoxicology laboratory of CETESB (Environmental Agency of São Paulo State) are accredited to ABNT-NBR ISO/IEC 17025 (equivalent national standard for ISO/IEC 17025:2005), which requires the estimative of the uncertainty of measurement associated with numerical results. As these analyses include living organisms, with variable individual sensitivity, the application of rigorous statistical procedures to estimate this uncertainty is troublesome and questionable. To compare some alternative approaches currently proposed for the evaluation of uncertainty related to ecotoxicological assays, an exercise was carried out with *Daphnia similis* data. These additional methods comply with EURACHEM/CITAC principles and include proficiency studies and interlaboratory reproducibility. Each of these two procedures resulted in distinct uncertainty values and confirmed that the total variance of biological response is controlled by the sample characteristics and concentrations analysed, as mentioned by other authors. Beside that, it is required the uncertainty of toxicity tests should be stablished for each sample through duplicate analyses, which would be an expensive and hard work approach. In view of such limitations, the laboratory decided to follow the CAEAL procedure (Canada, that meet the requirements of ISO/IEC 17025) and report the 95% confidence limits generated by specific softwares for each endpoint and particular test. Such confidence interval has the probability of containing the true value around the point estimate (LC, EC or IC), describing how reliable is the estimative as its width reflects the biological variability, the experimental design and the test performance.

Current situation and research needs for ecotoxicological assessment of pesticides in aquatic and terrestrial ecosystems

107 Research needs to improve ecological risk assessment in Brazil

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Since 2010 there is an effort to implement the risk evaluation of pesticides at Brazilian Institute for the Environment and Renewable Natural Resources – Ibama. Currently, only new active ingredients and active ingredients submitted to the process of reevaluation are evaluated considering procedures of risk assessment of pesticides. In 2015 Ibama created two Working Groups to discuss and develop clear and scientifically-based schemes of risk assessment to pollinators and aquatic organisms to be adopted in Brazil. These groups are coordinated by Ibama and are composed of members from government, academia and industry. At first, general and specific protection goals for maintenance of ecosystem services related to insect pollinators and to aquatic organisms were established. However, there are gaps in knowledge and research needs to ensure that procedures related to pesticides registry will be able to provide appropriate protection of crops without unacceptable risks to those non-target organisms. Some of the main gaps are: how native species are sensitive to pesticides, in what extension standard species can be used as good surrogates to protect native species, what are the levels of exposure in Brazilian scenarios and how the exposure routes can be different for the native species. Some of the information that could fill in these gaps could be provided by construction of SSD's curves for native species and pesticides of different modes of action, residue studies in relevant matrices to the non-target organisms, monitoring of water bodies located near agricultural crops, geo-referenced data regarding monitoring of Brazilian soils with description of soil characterization and validation of spray drift models. To provide these information and may be able to improve the process and reduce the uncertainty, it is necessary the generation of data, which only can be provided by basic research. Even facing these uncertainties, Ibama published in february the Normative Instruction 02/2017 that establishes procedures to risk assessment of pesticides to pollinators. The risk assessment process, that is dynamic and based on science, was developed on available information so far. The main intention of disclosure these gaps is to stimulate scientific research related to these topics, considering that Brazilian scientific community could fill and generate data under Brazilian conditions which will subsidizes environmental risk assessment and regulatory decision making.

108 Ecotoxicological impacts of pesticides to soil organisms

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Brazil is the largest consumer of pesticides in the world since 2008. The use of pesticides has increased 288% from 2000 to 2012. According to the Food and Agriculture Organization (FAO), by 2050 the world's population will increase 34% from today reaching 9.1 billion people. About 70% of the world's population will be urban (compared to 49 percent today). In order to feed this larger and urban population, food production (i.e. food used for biofuel, human and animal nutritions – cereals and meat) will have to be a lot improved. Hence, the growing demand for the increase of food production has led producers to seek alternatives to improve productivity using, many times, excessive amounts of pesticides and fertilizers. The effects caused to terrestrial ecosystem by the excessive pesticides and fertilizers applied into soil are the most neglected, especially in tropical and or subtropical countries. Information used to assess the risk of the pesticides use in tropical terrestrial ecosystem are usually taken from data obtained in temperate regions. European data do not always express the reality in tropical regions (i.e different climate conditions and soil properties) and so the results may not be always trusted. To solve this problem, specialists in soil ecotoxicology and ecology in Brazil are strongly influencing Brazilian researchers to run experiments in tropical conditions and use natural soils to evaluate ecotoxicological effects of pesticides to terrestrial organisms. Thus, the main goal of this study is to review data generated in Brazil regarding pesticides effects on terrestrial ecosystems, show some important results and propose further investigations on the theme.

109 Feeding activity of soil fauna after herbicide application: effects of glyphosate formulations measured by bait-lamina test

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Soil fauna plays an important role in regulating nutrient cycling through predation and fragmentation of organic residues. The bait-lamina test was proposed as a practical method to assess soil faunal feeding activity. This work aimed to evaluate the feeding activity of soil fauna after the application of four commercial glyphosate herbicides, Roundup Original(R), Trop(R), Zapp QI 620(R) e Crucial(R), to desiccate black oat. The recommended dose (720 g ha-1 acid equivalent, for each product evaluated) was applied for this purpose at the Experimental Farm of Federal University of Santa Catarina (UFSC), in Curitibanos, SC, Brazil, in three plots per treatment. As Controls were used three plots without application of herbicides. The bait lamina test (ISO 18311, 2016) consisted of vertically inserting 16-hole-bearing plastic strips filled with 70% cellulose, 25% wheat flour and 5% activated charcoal. The baits were exposed in situ at the 5th day after the herbicide applications, in November 2016, being three groups of eight baits per plot (2 x 2 m), inserted in three plots per treatment. After 40 days of exposure, the percentage of consumption was determined by recording the number of empty holes. Results from treatments were compared to Control using ANOVA followed by Dunnet?s test ($p< 0.05$). The mean consumption in Control was 63.4% (?10.7), Roundup Original(R) was 69.2% (?25.9), Trop(R) was 57.7% (?2.2), Zapp(R) was 68.2% (?13.8), and Crucial(R) was 37.9% (?7.0), being this last one significant lower than the Control ($p< 0.05$). Among these herbicides, Crucial(R) is the only one belonging to toxicological level I, red label, considered extremely toxic according to Brazil National Health Surveillance Agency (ANVISA). The other belong to level III, blue label, considered moderately toxic. Result indicated significant reduction of feeding activity in plots where Crucial(R) was applied, which can indicate impairment to ecosystem functions such as nutrient cycling. Further studies should be carried out to identify which groups of soil fauna are affected by this product. Funding: AGRISUS and Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq), Brasil, Projeto Universal CNPq 454842/2014-7.

110 Do agrochemicals pose a significant threat to biodiversity in sugarcane-producing landscapes?

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The environmental benefits of a global adoption of biofuels is critically contingent on which, where and how biofuel feedstocks are produced. Sugarcane is the most energetically efficient first-generation source of ethanol, yielding over eight units of biofuel energy output per-unit energy input when compared with two for beet, wheat, or corn. Brazil responds to 35% of the global production of sugarcane with 9.7 million hectares of cropland expanding over two of the world's biodiversity hotspots – the Atlantic Forest and Cerrados. Nevertheless, there is surprisingly little knowledge on the biodiversity consequences of sugarcane production in general, and of agrochemical management in particular. Sugarcane as a crop is the third largest consumer of pesticides in Brazil, in turn the largest pesticide consumer in the world. By 2010 there were 62 active ingredients registered for the management of sugarcane pests in the country, of which 5 cholinesterase inhibitors, 8 reprotoxic, 37 known, potential or suspected endocrine disruptors and 9 known or probable carcinogens. Of further potential ecotoxicological relevance are inorganic fertilizers and vinasse, a byproduct of sugarcane molasses distillation that is sprayed in sugarcane fields as an organic fertilizer. Pattern analysis indicates large increases in freshwater productivity and moderate levels of freshwater biodiversity (including amphibians and predatory aquatic insects) in sugarcane fields. However, occasional tadpole dieoffs in sugarcane drainage ponds have been witnessed and ammonia concentrations measured in the field, and herbicides applied at doses recommended by the manufacturers, are sufficient to elicit lethal and/or sublethal effects in native amphibian species in prolonged exposure in the lab. Considering that a significant share of pesticide applications occur outside of the rainy season and most published research efforts are biased towards freshwater systems, impacts of land management on terrestrial communities, and on the terrestrial phases of semiaquatic species with complex life cycles may be currently underestimated.

111 A first approach for the prioritization of pesticides for aquatic life protection in Brazil

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The process of approval of pesticides in Brazil is still based on hazard evaluation, but there is an effort going on for the implementation of risk assessment in this process. But until we do not have this process fully implemented it is important to provide information on the risk of the pesticides already in use. For that it is necessary to have data on occurrence of pesticides in national waters. But before that, we need to establish which compounds should be included in the monitoring programs. It is not possible to monitor 380 active ingredients approved for use in the country crops. This work presents a preliminary prioritization process based on tonnage of commercialized pesticides, followed by the comparison with the regulated pesticides