an antagonistic process, the volatilization of unaltered parathion-methyl from surfaces generally decreased in the presence of light, particularly in combination with increasing O_3 concentrations.

81.
PESTICIDE HANDLER EXPOSURE: DAY-TO-DAY URINE BIOMONITORING OF COMMERCIAL APPLICATORS. ***Travis M. Dinoff, Craig E. Bernard,*** *Marcella Oliver,* ***Ryan L. Williams,*** *and* ***Robert I. Krieger,*** *Department of Entomology, University of California, Riverside, Personal Chemical Exposure Program, Riverside, CA 92521, Fax: 909-787-5803, bob.krieger@ucr.edu, cbernard@ucrac1.ucr.edu, ryanw@citrus.ucr.edu, bob.krieger@ucr.edu*

Pesticide handlers are exposed to small amounts of active ingredients during normal day-to-day work tasks. Pesticides used included chlorpyrifos, carbaryl and 2,4-D. Urine samples were spiked with an internal standard of stable isotope labeled trichloropyridinol, 1-naphthol, and 2,4-D, acidified and heated for 1.5 hours, and then extracted with dichloromethane. The DCM extract was concentrated, reacted overnite with diazomethane in ether, reconcentrated and then analyzed by full scan 70 eV EI GC/MS. Extracted ions were used to quantitate equivalent chlorpyrifos, carbaryl, and 2,4-D. Simultaneous measurement is feasible when warranted. Day-to-day monitoring of 2 to 4 commercial applicators recorded low levels of pesticide equivalents relative toxic levels. Each biomarker was cleared rapidly alone or in combination with other metabolites. First tier exposure estimates using the Pesticide Handlers Exposure Database may be unduly inflated due to equipment and previous work practices, and methods used to monitor exposure. Representative and responsible risk assessment requires exposure estimates developed using biomonitoring whenever feasible.

82. 20033650
USE OF A HUMAN MICROSOMAL LIBRARY FOR METABOLITE ELUCIDATION, ASSAY DEVELOPMENT AND BIOLOGICAL MONITORING OF OCCUPATIONALLY RELEVANT COMPOUNDS. ***Cynthia A. F. Striley,*** *John E. Snawder, and Raymond E. Biagini, Biomonitoring and Health Assessment Branch, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Mailstop C-26, Cincinnati, OH 45226, Fax: 513-533-8510, chs3@cdc.gov*

Immunochemical biomonitoring is an effective tool for assessing exposure to agrochemicals. Effective biomonitoring requires knowledge of agent-specific human pharmacokinetics. We have procured a library of human tissue subfractions (hepatic, renal, pulmonary and jejunal) to serve as an invitro surrogate of human metabolism. Characterization of these tissues for Phase I and Phase II metabolic enzymes has been performed to elucidate variation in metabolism. The impact of individual variation on the metabolism of occupational/environmental chemicals can be estimated by accurately quantifying the expression of the pertinent enzyme(s) in human tissues. These data can be combined with data describing the specific activity of CYP forms towards substrates to develop metabolic rates, and their ranges, useful for the development of suitable biomarkers to estimate exposure to xenobiotics. Microsomal assay and HPLC analysis was used to determine human metabolism of azinphosmethyl, piperalin and bromopropane. Candidate biomarkers were then used to develop ELISAs for urinary analysis.

83.
STEROL COMPOUNDS IN AGRICULTURAL RUNOFF INTO CHESAPEAKE BAY TRIBUTARIES. ***Thomas B. Huff***[1]*, Gregory D. Foster*[2]*, Cherie V. Miller*[3]*, and Kimberly Lauer*[2]*. (1) Shared Research Instrumentation Facility, George Mason University, 4400 University Drive, Fairfax, VA 22030, Fax: 703 993-4581, thuff@gmu.edu, (2) Department of Chemistry, George Mason University, (3) Water Resources Division, USGS*

Excess nutrient enrichment in the Pocomoke River, Maryland may contribute to oxygen depletion and other extreme ecological conditions leading to an outbreak of Pfiesteria pisicida and subsequent fish kills. This nutrient enrichment is suspected to result from manure runoff from local agricultural operations. High concentrations of specific enteric sterols can indicate agricultural manure contamination in watersheds. Enteric sterols may serve as biomarkers indicating specific sources of fecal contamination. These biomarkers may also delineate the transport of other agrochemicals throughout the watershed. Pocomoke River water and sediment samples and chicken manure samples were extracted and analyzed by GC-MS for 11 sterols. Profiles of sterol concentrations and ratios of specific sterols showed similarities between the sediment samples and the chicken manure. Cholesterol levels in water samples showed a concentration gradient upstream towards poultry operations indicating that sterols may be useful biomarkers for other agrochemicals.

84.
ARTIFACT IMPURITIES FOUND IN GRADIENT HPLC ANALYSIS: EFFECT OF THE REAGENT SOURCE AND QUALITY ON THE NUMBER AND CONCENTRATION OF ARTIFACT IMPURITIES. ***Kenneth J. Norris Jr.,*** *Beverly Nickerson, and Suzette Izquierdo, Analytical Research & Development, Pfizer Inc, Eastern Point Road, Bldg 118 Box 4005, Groton, CT 06340, Fax: 860-715-8425, kenneth_j_norris@groton.pfizer.com*

The use of gradient HPLC in potency, purity and bioanalytical analysis has increased. The performance of a gradient HPLC analysis depends on running clean blank chromatograms. The source of the solvents and reagents greatly affects the performance of these gradient methods no matter what method of detection is used. This work utilized blank gradients to screen solvents and mobile phase modifiers for impurities. The solvent program used an isocratic hold followed by a gradient sweep. Water from several suppliers as well as Milli-Q water from our laboratory were evaluated. Buffering agents such as TFA, perchloric acid, ammonium acetate, phosphoric acid and organic solvents were also studied. The results of these screens and possible methods for cleaning the mobile phase will be presented.

85.
APPLICATION OF AN IMMUNOAFFINITY COLUMN AS A SAMPLE CLEANUP METHOD FOR THE ß-ADRENERGIC AGONIST RACTOPAMINE AND ITS METABOLITES. ***Weilin L. Shelver,*** *and David J. Smith, Biosciences Research Laboratory, USDA-ARS, 1605 Albrecht Boulevard, Fargo, ND 58105, Fax: 701-239-1430, shelverw@fargo.ars.usda.gov*

A monoclonal antibody based immunoaffinity column (RAC-IAC) was developed as a potential "cleanup" method for ractopamine and ractopamine-glucuronides. [14C]Ractopamine (5 µg) and [14C]ractopamine-glucuronides (5 µg) were spiked into 10 mL of control urine, loaded onto a column (5 mg IgG/1mL), and eluted with 10 mL of 50% aqueous methanol followed by 10 mL of 100% methanol. The RAC-IAC retained 78% of the applied radioactivity; and 22% was not retained. HPLC analysis of the 50% MeOH fraction contained an approximately equal mixture of ractopamine and ractopamine-glucuronides. The 100% MeOH fraction contained predominately ractopamine. By comparison, 92% of the radioactivity loaded onto a non-specific IAC did not bind. A ractopamine IAC has the potential to be a selective, efficient, and economical cleanup method for use in ractopamine analyses.

86.
DEVELOPMENT OF AN ELISA FOR THE HERBICIDE ISOXAFLUTOLE. ***Jeremy J. Brandl***[1]*, Diana S. Aga*[1]*, Karl Kramer*[2]*, and Bertold Hock*[2]*. (1) Department of Chemistry, University of Nebraska at Kearney, 905 W. 25th St, Kearney, NE 68849, Fax: 308-865-8399, jbrandl@unk.edu, (2) Botany, Technical University of Munich*

This study involves the development of an enzyme-linked immunosorbent assay (ELISA) technique for the detection of a newly registered herbicide, isoxaflutole. The high water solubility of isoxaflutole and its primary and secondary metabolites poses a high potential for ground and surface water contamination. Polyclonal antibodies were produced in rabbits that were immunized with the polylysine conjugates of the secondary metabolite of isoxaflutole. The antibodies were therefore most sensitive towards the secondary metabolite. Direct and indirect ELISAs were compared using either biotinylated analytes, HRP-conjugated analytes, or BSA-conjugated analytes for competitive immunochemical reaction. Indirect ELISA format shows the best sensitivity for the secondary metabolite.

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