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CHEMICAL EFFECTS

Comparison of the extractability of organophosphorus flame retardants in landfill media using organic and green solvents

2022-06-09

Organic solvents are mainly used in the extraction of organophosphorus flame retardants (OPFRs) because of their availability and having been tested as good extracting solvents for most environmental pollutants. However, organic solvents are toxic, flammable, and costly. Hence, there is an ongoing quest for less hazardous chemicals such as green deep eutectic solvents (DES) that are cheap, recyclable, non-toxic and degradable in the environment, which can be used to extract organic pollutants such as OPFRs in environmental samples. This study assessed the extractability of OPFRs in municipal landfill leachate and sediment, using organic solvents and DES. Of the fourteen targeted OPFRs, 11 (80%) and 7 (50%) were detected in the leachate and sediment samples, using hexane; whereas 14 (100%) and 13 (90%) OPFRs were detected in the same order of samples using DES. The concentrations of OPFRs obtained for the leachate using optimum organic and DES ranged from below the limit of quantification ($< \text{LOQ}$)- 516 ± 8.10 ng/L and $< \text{LOQ}$ - 453 ± 8.10 ng/L respectively. Correspondingly, the concentrations of OPFRs in sediment samples ranged from $< \text{LOQ}$ - 135 ± 2.89 ng/g dw and $< \text{LOQ}$ - 395 ± 2.24 ng/g dw, respectively. The results from this study, therefore, highlight the potential of DES to extract more OPFR from complex matrices such as landfill leachate and sediment. This finding infers that green hydrophilic DES can serve as good replacement for organic solvents such as hexane in liquid-liquid extraction (LLE) and solid-liquid extraction (SLE) techniques for landfill leachate and sediment.

Authors: Innocentia Velaphi Sibiyi, Okechukwu Jonathan Okonkwo

Full Source: Scientific reports 2022 Jun 9;12(1):9529. doi: 10.1038/s41598-022-13704-1.

Genotoxicity of Graphene-Based Materials

2022-05-24

Graphene-based materials (GBMs) are a broad family of novel carbon-based nanomaterials with many nanotechnology applications. The increasing market of GBMs raises concerns on their possible impact on human health. Here, we review the existing literature on the genotoxic potential of GBMs over the last ten years. A total of 50 articles including

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in vitro, in vivo, in silico, and human biomonitoring studies were selected. Graphene oxides were the most analyzed materials, followed by reduced graphene oxides. Most of the evaluations were performed in vitro using the comet assay (detecting DNA damage). The micronucleus assay (detecting chromosome damage) was the most used validated assay, whereas only two publications reported results on mammalian gene mutations. The same material was rarely assessed with more than one assay. Despite inhalation being the main exposure route in occupational settings, only one in vivo study used intratracheal instillation, and another one reported human biomonitoring data. Based on the studies, some GBMs have the potential to induce genetic damage, although the type of damage depends on the material. The broad variability of GBMs, cellular systems and methods used in the studies precludes the identification of physico-chemical properties that could drive the genotoxicity response to GBMs.

Authors: Josefa Domenech, Adriana Rodríguez-Garraus, Adela López de Cerain, Amaya Azqueta, Julia Catalán

Full Source: Nanomaterials (Basel, Switzerland) 2022 May 24;12(11):1795. doi: 10.3390/nano12111795.

ENVIRONMENTAL RESEARCH

Adsorption, Structure, and Dynamics of Short- and Long-Chain PFAS Molecules in Kaolinite: Molecular-Level Insights

2022-05-11

The ubiquitous presence of poly- and perfluoroalkyl substances (PFAS) in different natural settings poses a serious threat to environmental and human health. Soils and sediments represent one of the important exposure pathways of PFAS for humans and animals. With increasing bioaccumulation and mobility, it is extremely important to understand the interactions of PFAS molecules with the dominant constituents of soils such as clay minerals. This study reports for the first time the fundamental molecular-level insights into the adsorption, interfacial structure, and dynamics of short- and long-chain PFAS molecules at the water-saturated mesopores of kaolinite clay using classical molecular dynamics (MD) simulations. At environmental conditions, all the PFAS molecules are exclusively adsorbed near the hydroxyl surface of the kaolinite, irrespective of the terminal functional groups and metal cations. The interfacial adsorption structures and coordination environments of PFAS are strongly dependent on the nature of the functional groups and their hydrophobic chain length. The formation of large, aggregated clusters of

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long-chain PFAS at the hydroxyl surface of kaolinite is responsible for their restricted dynamics in comparison to short-chain PFAS molecules. Such comprehensive knowledge of PFAS at the clay mineral interface is critical to developing novel site-specific degradation and mitigation strategies.

Authors: Narasimhan Loganathan and Angela K. Wilson

Full Source: Environmental Science & Technology 2022 May 11. doi: 10.1021/acs.est.2c01054.

Aminocatalysts are more environmentally friendly than hydrogen-bonding catalysts

2022-06-10

The importance of asymmetric organocatalysis in contemporary organic synthesis is widely acknowledged. However, there are practically no data on the environmental safety of organocatalysts, although this aspect is crucial for the sustainability of all new materials/chemicals/technologies. To start to fill this data-gap, a library of 26 organocatalysts containing hydrogen bonding catalysts ((thio)ureas and squaramides) and aminocatalysts (primary or secondary amines) was evaluated for their toxicity using the naturally luminescent *Vibrio fischeri* bacteria (an ISO assay - one of the most widely used ecotoxicity tests). We showed that thioureas and squaramides were relatively toxic: none of them was ranked as "not harmful" (i.e. EC 50 >100 mg/L) whereas the presence of the trifluoromethyl moiety increased their toxic effect. Importantly, the aminocatalysts whose EC 50 values ranged from 25 to >300 mg/L could be considered remarkably more environmentally safe or green alternatives.

Authors: Mariliis Sihtmäe, Estelle Silm, Kadri Kriis, Anne Kahru, Tõnis Kanger
Full Source: ChemSusChem 2022 Jun 10. doi: 10.1002/cssc.202201045.

PM 2.5 air pollution exposure and nonalcoholic fatty liver disease in the Nationwide Inpatient Sample

2022-06-07

Background: Nonalcoholic fatty liver disease (NAFLD) is the most common cause of chronic liver disease. Particulate matter air pollution <2.5 μm in diameter (PM2.5) is a ubiquitous exposure primarily produced from fossil fuel combustion. Previous epidemiologic studies have been mixed. The objective of this study was to examine the association between ambient PM2.5 exposure and NAFLD among hospitalized patients in the Nationwide Inpatient Sample (NIS). Methods: We conducted a cross-sectional analysis of hospitalizations from 2001 to 2011 using the NIS, the largest nationally representative all-payer inpatient

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care administrative database in the United States. Average annual PM2.5 exposure was estimated by linking census tracts (based on NIS-provided hospital ZIP Codes) with a spatiotemporal exposure model. Clinical conditions were identified using hospital discharge diagnosis codes. Multivariable logistic regression incorporating discharge weights was used to calculate odds ratios (ORs) and 95% confidence intervals (CIs) for the association between PM2.5 exposure and odds of NAFLD among hospitalized patients adjusting for age, sex, race/ethnicity, year, individual- and area-level socioeconomic status, urbanicity, region, obesity, diabetes, metabolic syndrome, impaired fasting glucose, dyslipidemia, hypertension, obstructive sleep apnea, and smoking. Results: There were 269,705 hospitalized patients with NAFLD from 2001 to 2011 (total unweighted n = 45,433,392 hospitalizations). Higher ambient PM2.5 exposure was associated with increased odds of NAFLD among hospitalized patients (adjusted OR: 1.24 per 10 μg/m³ increase, 95% CI 1.15-1.33, p < 0.01). There were statistically significant interactions between PM2.5 exposure and age, race/ethnicity, diabetes, smoking, and region, with stronger positive associations among patients who were aged ≥45 years, non-Hispanic White or Asian/Pacific Islander, non-diabetics, non-smokers, or in the Midwest and West regions, respectively. Conclusions: In this nationwide cross-sectional analysis of the NIS database, there was a positive association between ambient PM2.5 exposure and odds of NAFLD among hospitalized patients. Future research should examine the effects of long-term historical PM2.5 exposure and incident NAFLD cases.

Authors: Trang VoPham, Nicole J Kim, Kristin Berry, Jason A Mendoza, Joel D Kaufman, George N Ioannou
Full Source: Environmental research 2022 Jun 7;113611. doi: 10.1016/j.envres.2022.113611.

Exposure to organophosphorus pesticides may lead to reproductive hormone dysfunction.

PHARMACEUTICAL/TOXICOLOGY

Alterations in reproductive hormone levels among farm women and their children occupationally exposed to organophosphate pesticides

2022-06

Exposure to organophosphorus pesticides may lead to reproductive hormone dysfunction. Even among children of pubertal age, the exposure may disrupt growth, development, and maturation. The present study was conducted to assess the alterations in the reproductive hormone

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levels, among farm women (24-45 years, n = 129) and their children (9-12 years, n = 66 and 13-15 years, n = 63) and compare them with age and gender-matched control group [women (n = 134) and their children (9-12 years, n = 69 and 13-15 years, n = 65)] belonging to villages of Ranga Reddy District, Telangana, India. Blood pesticide residues and reproductive hormone (follicle-stimulating hormone-FSH, luteinizing hormone-LH, estradiol, and testosterone) levels were analyzed. The detected pesticide residues (ng/mL) were chlorpyrifos, diazinon, malathion, and monocrotophos among the farm women, while the farm children of 9-12 years age groups were detected with residues of chlorpyrifos, diazinon, malathion, monocrotophos, and phosalone. The farm children of 13-15 years age group were detected with residues of chlorpyrifos, diazinon, malathion, monocrotophos, and phosalone. However, no residues were detected among the samples of women and children of control groups. Significantly lower levels of FSH (in follicular phase) were observed among the farm women than the control group. Significant alterations in FSH and LH levels of farm women were observed with a significant correlation between the chlorpyrifos residue levels and estradiol hormone. While no such significant change in hormone levels was observed among the farm children of both age groups of both genders. Though the present study showed pesticide-induced alterations in hormone levels among the farm women, research is needed to elucidate the critical windows during which exposure may adversely affect the reproductive system in children at the pubertal stage and women at reproductive age and subsequently their progeny's health at a later stage of life.

Authors: Srujana Medithi, Yogeswar Dayal Kasa, Babban Jee, Kodali Venkaiah, Padmaja R Jonnalagadda

Full Source: *Women & health* May-Jun 2022;62(5):454-464. doi: 10.1080/03630242.2022.2085844.

Meta-analysis of epigenome-wide association studies in newborns and children show widespread sex differences in blood DNA methylation

2022-06

Background: Among children, sex-specific differences in disease prevalence, age of onset, and susceptibility have been observed in health conditions including asthma, immune response, metabolic health, some pediatric and adult cancers, and psychiatric disorders. Epigenetic modifications such as DNA methylation may play a role in the sexual differences observed in diseases and other physiological traits. **Methods:** We performed a meta-analysis of the

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association of sex and cord blood DNA methylation at over 450,000 CpG sites in 8438 newborns from 17 cohorts participating in the Pregnancy And Childhood Epigenetics (PACE) Consortium. We also examined associations of child sex with DNA methylation in older children ages 5.5-10 years from 8 cohorts (n = 4268). **Results:** In newborn blood, sex was associated at Bonferroni level significance with differences in DNA methylation at 46,979 autosomal CpG sites ($p < 1.3 \times 10^{-7}$) after adjusting for white blood cell proportions and batch. Most of those sites had lower methylation levels in males than in females. Of the differentially methylated CpG sites identified in newborn blood, 68% (31,727) met look-up level significance ($p < 1.1 \times 10^{-6}$) in older children and had methylation differences in the same direction. **Conclusions:** This is a large-scale meta-analysis examining sex differences in DNA methylation in newborns and older children. Expanding upon previous studies, we replicated previous findings and identified additional autosomal sites with sex-specific differences in DNA methylation. Differentially methylated sites were enriched in genes involved in cancer, psychiatric disorders, and cardiovascular phenotypes.

Authors: Olivia Solomon, Karen Huen, Paul Yousefi, Leanne K Küpers, Juan R González, Matthew Suderman, Sarah E Reese, Christian M Page, Olena Gruzieva, Peter Rzehak, Lu Gao, Kelly M Bakulski, Alexei Novoloaca, Catherine Allard, Irene Pappa, Maria Llambrich, Marta Vives, Dereje D Jima, Tuomas Kvist, Andrea Baccarelli, Cory White, Faisal I Rezwan, Gemma C Sharp, Gwen Tindula, Anna Bergström, Veit Grote, John F Dou, Elena Isaevska, Maria C Magnus, Eva Corpeleijn, Patrice Perron, Vincent W V Jaddoe, Ellen A Nohr, Lea Maitre, Maria Foraster, Cathrine Hoyo, Siri E Håberg, Jari Lahti, Dawn L DeMeo, Hongmei Zhang, Wilfried Karmaus, Inger Kull, Berthold Koletzko, Jason I Feinberg, Luigi Gagliardi, Luigi Bouchard, Cecilia Høst Ramlau-Hansen, Henning Tiemeier, Gillian Santorelli, Rachel L Maguire, Darina Czamara, Augusto A Litonjua, Jean-Paul Langhendries, Michelle Plusquin, Johanna Lepeule, Elisabeth B Binder, Elvira Verduci, Terence Dwyer, Ángel Carracedo, Natalia Ferre, Brenda Eskenazi, Manolis Kogevinas, Tim S Nawrot, Monica C Munthe-Kaas, Zdenko Herceg, Caroline Relton, Erik Melén, Dariusz Gruszfeld, Carrie Breton, M D Fallin, Akram Ghantous, Wenche Nystad, Barbara Heude, Harold Snieder, Marie-France Hivert, Janine F Felix, Thorkild I A Sørensen, Mariona Bustamante, Susan K Murphy, Katri Raikkönen, Emily Oken, John W Holloway, Syed Hasan Arshad, Stephanie J London, Nina Holland
Full Source: *Mutation research. Reviews in mutation research* Jan-Jun 2022;789:108415. doi: 10.1016/j.mrrev.2022.108415.

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OCCUPATIONAL

Citizens' Perception and Concerns on Chemical Exposures and Human Biomonitoring-Results from a Harmonized Qualitative Study in Seven European Countries

2022-05-25

Exposure to different chemicals is an inevitable part of our everyday lives. Within HBM4EU, focus group discussions were conducted to gather data on citizens' perceptions of chemical exposure and human biomonitoring. These discussions were hosted in Cyprus, Denmark, Hungary, Israel, Latvia, the Netherlands, and North Macedonia following a protocol developed in the first round of discussions. Results indicate the very high concern of European citizens regarding food safety and the environment. Focus group participants were well aware of potential uptake of chemicals through food consumption (e.g., preservatives, flavor enhancers, coloring agents, pesticides, fertilizers, metals), drinking water, or from polluted air and water. One of the positive aspects identified here, is the high interest of citizens in awareness and education on personal measures to control exposure. The promotion of personal behavioral changes requires active involvement of society (e.g., commuting habits, energy choices, waste disposal, dietary habits). Activities should focus on raising awareness of the general public, implementation of policy measures, and mainstreaming of related topics into the education system. Raising awareness of the general public may promote engagement of citizens, which in turn may empower them to put pressure on politicians to take effective actions. There is also a need for further research which might focus on the impact of country-specific situations and of the COVID-19 pandemic on the exposure of citizens to chemicals.

Authors: Linda Matisāne, Lisbeth E Knudsen, Joana Lobo Vicente, Maria Uhl, Andromachi Katsonouri, Annick D van den Brand, Tamar Berman, Mirjana Dimovska, Eleni Anastasi, Anthi Thoma, Szilvia Középesy, Dragan Gjorgjev, Mirjana Borota Popovska, Shalenie P den Braver-Sewradj, Tamás Szigeti, Marija Topuzovska Latkovikj, Inese Mārtiņšone, Lāsma Akūlova, Linda Paegle

Full Source: International journal of environmental research and public health 2022 May 25;19(11):6414. doi: 10.3390/ijerph19116414.

Exposure to different chemicals is an inevitable part of our everyday lives.

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Characterization of Exposure to Cleaning Agents Among Health Workers in Two Southern African Tertiary Hospitals

2022-06-08

Background: Whilst cleaning agents are commonly used in workplaces and homes, health workers (HWs) are at increased risk of exposure to significantly higher concentrations used to prevent healthcare-associated infections. Exposure assessment has been challenging partly because many are used simultaneously resulting in complex airborne exposures with various chemicals requiring different sampling techniques. The main objective of this study was to characterize exposures of HWs to various cleaning agents in two tertiary academic hospitals in Southern Africa. **Methods:** A cross-sectional study of HWs was conducted in two tertiary hospitals in South Africa (SAH) and Tanzania (TAH). Exposure assessment involved systematic workplace observations, interviews with key personnel, passive personal environmental sampling for aldehydes (ortho-phthalaldehyde-OPA, glutaraldehyde and formaldehyde), and biomonitoring for chlorhexidine. **Results:** Overall, 269 samples were collected from SAH, with 62 (23%) collected from HWs that used OPA on the day of monitoring. OPA was detectable in 6 (2%) of all samples analysed, all of which were collected in the gastrointestinal unit of the SAH. Overall, department, job title, individual HW use of OPA and duration of OPA use were the important predictors of OPA exposure. Formaldehyde was detectable in 103 (38%) samples (GM = 0.0025 ppm; range: <0.0030 to 0.0270). Formaldehyde levels were below the ACGIH TLV-TWA (0.1 ppm). While individual HW use and duration of formaldehyde use were not associated with formaldehyde exposure, working in an ear, nose, and throat ward was positively associated with detectable exposures (P-value = 0.002). Glutaraldehyde was not detected in samples from the SAH. In the preliminary sampling conducted in the TAH, glutaraldehyde was detectable in 8 (73%) of the 11 samples collected (GM = 0.003 ppm; range: <0.002 to 0.028). Glutaraldehyde levels were lower than the ACGIH's TLV-Ceiling Limit of 0.05 ppm. p-chloroaniline was detectable in 13 (4%) of the 336 urine samples (GM = 0.02 ng/ml range: <1.00 to 25.80). **Conclusion:** The study concluded that detectable exposures to OPA were isolated to certain departments and were dependent on the dedicated use of OPA by the HW being monitored. In contrast, low-level formaldehyde exposures were present throughout the hospital. There is a

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need for more sensitive exposure assessment techniques for chlorhexidine given its widespread use in the health sector.

Authors: H H Mwanga, R Baatjies, M F Jeebhay

Full Source: *Annals of work exposures and health* 2022 Jun 8;wxac034. doi: 10.1093/annweh/wxac034.

The Dangers of Reused Personal Protective Equipment: Healthcare Workers and Workstation Contamination

2022-06-07

Personal protective equipment is essential to protect healthcare workers (HCW). The practice of using reused personal protective equipment (PPE) poses high levels of risk for accidental contamination by healthcare workers. Scarce medical literature compares practical means or methods for safe PPE reuse while actively caring for patients. We observed 28 experienced clinical participants perform five donning and doffing encounters while performing simulated full COVID-19 patient evaluations. Participant N95 respirators were coated with a fluorescent dye to evaluate any accidental fomite transfer that occurred during PPE donning and doffing. Participants were evaluated using a blacklight after each doffing encounter to evaluate for new contamination sites and were assessed for the cumulative surface area that occurred due to PPE reuse doffing. Additionally, the participant's workstations were evaluated for contamination. All participants experienced some amount of contamination to their upper extremities, neck, and face. The highest cumulative area of fomite transfer risk was associated with the hook and paper bag storage methods, and the least contamination occurred with the tabletop respirator storage method. We found that storing a reused N95 respirator on a tabletop is a safer alternative compared to the current CDC paper bag storage recommendations. All participants donning and doffing PPE were contaminated. The results suggest that the current design of PPE required improved engineering and usability. PPE reuse practices pose an unacceptably high level of risk of accidental cross infection contamination to healthcare workers.

Authors: Devin Doos, Paul Barach, Nathan J Alves, Lauren Falvo, Anna Bona, Malia Moore, Dylan D Cooper, Roxanna Lefort, Rami Ahmed

Full Source: *The Journal of hospital infection* 2022 Jun 7;S0195-6701(22)00170-0. doi: 10.1016/j.jhin.2022.05.016.

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