Association of Chemistry and
the Environment - ACE a.s.b.l.

# 1st Seminar of the Association of Chemistry and the Environment (ACE)

*17 -18 February 2021*

## Pollutants in the Environment

## Book of abstracts

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**1st ACE Seminar on Chemistry and the Environment (Pollutants in the Environment)** complements the well-established tradition of international conferences EMEC and covers a broad range of topics within the field of Pollutants in the Environment. This first seminar event includes lectures presented by young scientists from ACE board representatives centers.

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### Legend:

IL - Invited Lecture
O - Oral presentation

## PROGRAMME

### February 17, 2021

| Time | Lecturer | Title |
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| 14:30-14:55 | Lydia Niemi | Temporal and spatial trends in pharmaceutical concentrations in an effluent-receiving river |
| 14:55-15:20 | Piero Bellanova | How Indian urban rivers are affected by human impact - an example from Chennai |
| 15:20-15:45 | Coffee break | |
| 15:45-16:10 | Daqing Jia | Caffeine degradation in water by Mn2O3 activation of various radical precursors |
| 16:10-16:35 | Sabina Llamazares Vegh | Bioaccumulation of trace elements in freshwater juvenile fishes: implications associated with essential fish growing habitat |
| 16:35-17:00 | Luca Carena | Photochemistry of surface waters and climate change: possible effects of hydrological drought on the decontamination potential of water bodies from pollutants |

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| 14:25-14:50 | Franja Prosenc | Microalgae-based removal of contaminants of emerging concern |
| 14:50-15:15 | Anna Sosnova | GC-HRMS with Complimentary Ionization Techniques for Target and Nontarget Screening for Chemical Exposure: Expanding the Insights of the Air Pollution Markers in Moscow Snow |
| 15:15-15:40 | Francisco Sánchez-Soberón | The problematic of siloxanes in WWTPs and biogas production |
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| 16:05-16:30 | Manel Touihri | Development of novel magnetic composite $Fe_3O_4$/pine cones gel beads for heavy metals removal in simple and binary Systems |
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# INDEX OF ABSTRACTS

**IL 1**

# ISOTOPE RATIO MASS SPECTROMETRY IN ENVIRONMENTAL ANALYSIS

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Isotope ratio mass spectrometry (IRMS) is mass spectrometric method focused on the determination of relative abundance of stable isotopes in sample. Most often, ratios of $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{15}N/^{14}N$ and $^{2}D/^{1}H$ are measured.

Stable isotope ratios in various object are slightly different. For example, terrestrial relative abundance of $^{12}C$ and $^{13}C$ are 98,89 % and 1,11 %, respectively. Their ratio could be influenced by isotope fractionation during natural, chemical, climatic and anthropogenic processes. This isotopic fractionation is result of tiny differences in physical-chemical properties between isotopologues - e.g., $H_2{}^{16}O$ and $H_2{}^{18}O$ have boiling points at 101.325 kPa 100.00 °C and 100.14 °C, respectively, so $H_2{}^{16}O$ evaporates slightly faster than $H_2{}^{18}O$. The isotopic ratio can thus provide information, for example, on the origin of the sample or on the processes it has undergone in the past. Ratio of $^{13}C/^{12}C$ is influenced by different discrimination of $^{13}C$ during photosynthesis between plants of subtropical and temperate zone, which could be used for assessment of food origin. In the tree rings this ratio reflects the amount of precipitation during the tree growth. Ratio of $^{18}O/^{16}O$ reflects the altitude and also the temperature of concrete place. Ratio of $^{15}N/^{14}N$ is very useful for determining of the origin source of atmospheric pollution. It also allows the distinction between biogenic and synthetic fertilizers.

Mass spectrometers used in this field are almost exclusively equipped with low-resolution magnetic sector analyser and electron ionization. Array of Faraday cups is used for simultaneous detection of selected ion species. Analysed samples are converted (most often by burning or pyrolysis) to simple gaseous compounds which are then delivered to ion source (e.g. for the determination of $^{13}C/^{12}C$ ratio conversion to $CO_2$ followed by detection of m/z 44, 45 and 46, for the determination of $^{18}O/^{16}O$ ratio conversion to CO followed by detection of m/z 28, 29 and 30).

**O 1**

# TEMPORAL AND SPATIAL TRENDS IN PHARMACEUTICAL CONCENTRATIONS IN AN EFFLUENT-RECEIVING RIVER

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Pharmaceuticals (a class of emerging contaminants) are continuously introduced into effluent-receiving surface waters due to their incomplete removal within wastewater treatment plants (WWTPs). This work investigated the presence and distribution of eight commonly used human pharmaceuticals in the River Dee (Scotland, UK), a Scottish Environment Protection Agency priority catchment and conservation site that is under significant stress from growing urbanisation. Traditional grab sampling and novel passive sampling was performed over 12 months (once every three months), targeting: paracetamol, ibuprofen, and diclofenac (analgesics/anti-inflammatories); clarithromycin and trimethoprim (antibiotics); carbamazepine, fluoxetine (psychoactive drugs); and 17α-ethynylestradiol (estrogen hormone). There were eight sampling sites, spanning from the river's source to the estuary discharge into the North Sea. Passive samplers (Polar Organic Chemical Integrative Samplers, POCIS) were deployed over 14 days in the river, and grab sampling was performed on POCIS deployment and retrieval. Solid phase extraction and analysis with liquid chromatography-tandem mass spectrometry enabled quantification of pharmaceutical concentrations. Concentrations were most pronounced near WWTP discharge sites, and generally increased down river with increasing urbanisation. River flow data was assessed, revealing that low flow and warm seasons corresponded to statistically significantly higher concentrations of some compounds. Future work should continue monitoring pharmaceutical presence in the River Dee and estuary to establish environmental fate and risks related to unusual weather patterns and climate change.

**O 2**

# HOW INDIAN URBAN RIVERS ARE AFFECTED BY HUMAN IMPACT - AN EXAMPLE FROM CHENNAI

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Fast-growing mega cities, such as Chennai (India), fight an uphill battle in maintaining their increasingly urbanized drainage and riverine systems. The lack of regulations coinciding with growing volumes of sewage water and physical waste through the rising population have an enormous toll on these aquatic systems. Further do anthropogenic interferences (e.g., damming, dredging) and river regulation cause the interruption of principal transport processes and distribution of sediment- and water-bound natural organic compounds needed for a healthy ecosystem. These anthropogenic incisions also favour the increased introduction of organic contaminant (mainly through wastewater). This is intensified by the damming for water reservoirs upstream in combination with seasonality (monsoon and dry season) of the subtropical river systems, resulting in stagnant river conditions most of the year and the river's feeding originating mostly from wastewater inlets. Pollutants from urban and industrial wastewaters (e.g., PAHs, LABs, DPE, DEHA, NBFA, Mesamoll®) have been identified to be suitable markers to assess the anthropogenic induced pollution and chemostratigraphic evolution of these river systems. However, the given sedimentary archives in these fast-growing and urbanized areas might not always allow a full reconstruction of the past, as anthropogenic alterations on the river's course and floodplains effect the archive's preservation potential. For Chennai, advantages and disadvantages regarding the chemostratigraphic preservation are delicately balanced. However, increasing urbanization and anthropogenic overprinting causes the disruption of sedimentary archives and redistribution of contaminated material (e.g., through dredging), this favours remobilization and relocation of hazardous contaminants.

**O 3**

# CAFFEINE DEGRADATION IN WATER BY $Mn_2O_3$ ACTIVATION OF VARIOUS RADICAL PRECURSORS

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Caffeine (CAF) is a stimulant commonly found in beverages and employed as the main component for producing prescription drugs. The discharging of CAF into environment pose a threat to aquatic environment and population health. Traditional water treatment technologies show a minimal effect on CAF removal. Therefore, it is necessary to develop an efficient water treatment technology for CAF degradation. $MnO_2$ based AOPs have received an increasing attention in organic pollutants treatment process. Moreover, the important role of Mn(III) species in $MnO_2$ oxidative and catalytic reactivity was highlighted. However, the studies employing manganese (III) oxide as the radical activator are rarely reported. In this study, $Mn_2O_3$ activation of various radical precursors ($H_2O_2$, PS, Oxone, $HSO_3^-$) for CAF degradation was investigated. The results showed that no CAF degradation was observed with the addition of $H_2O_2$ and $HSO_3^-$. In comparison, ~40% of CAF was removed by $Mn_2O_3$ and PS/Oxone in 3 hours under natural solution pH, indicating the generation of reactive radicals in $Mn_2O_3$ + PS/PMS systems. The results of this study provide a comprehensive understanding of the reactivity of $Mn_2O_3$ with various radical precursors.

**O 4**

# BIOACCUMULATION OF TRACE ELEMENTS IN FRESHWATER JUVENILE FISHES: IMPLICATIONS ASSOCIATED WITH ESSENTIAL FISH GROWING HABITAT

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Metal and metalloids accumulation in fish depends on both the chemical properties of the elements and different factors such as ecological needs, the physiological state, size and age of individuals, as well as the life history and feeding habits. This study assessed the concentration, bioconcentration, and bioaccumulation of As, Cd, Co, Cr, Cu, Mg, Mn, Ni, Pb, and Zn in juvenile fishes of several species in the Lower Paraná River (Argentina), the most extensive floodplain from the Plata Basin. The floodplain is crucial for the reproduction and growth of migratory species such as *Prochilodus lineatus*, *Megaleporinus obtusidens*, and *Salminus brasiliensis,* which complete their life cycle in this environment. Individuals were sampled for nitrogen stable isotope, and trace element analysis in muscle tissue, water, and sediment was analyzed. The results show that all the studied species bioaccumulate Cr, Mg, Ni, and Zn. In particular, *Brycon orbygnianus* and *Pimelodus maculatus* presented the highest bioaccumulation factor for Cr. A biodilution of Co through the food chain was observed. No positive correlation was found between element concentration and trophic level, but we observed significant differences between trophic guilds (herbivorous, omnivorous, and carnivorous). Our findings suggest that feeding habits determine trace element concentrations. Further studies are necessary to establish differential behavior between different species within the aquatic web, particularly in the floodplain of the Paraná, which is a crucial nursery area for most commercially important fishes from the Plata Basin.

**O 5**

# PHOTOCHEMISTRY OF SURFACE WATERS AND CLIMATE CHANGE: POSSIBLE EFFECTS OF HYDROLOGICAL DROUGHT ON THE DECONTAMINATION POTENTIAL OF WATER BODIES FROM POLLUTANTS

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Sunlight reaching surface freshwaters can be absorbed by the naturally occurring chromophoric dissolved organic matter (CDOM), with subsequent photoproduction of reactive species. These reactants, called *Photochemically Produced Reactive Intermediates* (PPRIs), are mainly $HO^{\bullet}$ and $CO_3^{\bullet-}$ radicals, triplet states of CDOM ($^3$CDOM*) and singlet oxygen ($^1O_2$).

PPRIs play an important role in the context of water (de)pollution, because they can trigger contaminants degradation. This process can be environmentally helpful, but in some cases it can lead to the photoproduction of compounds that are as toxic as or even more toxic than the parent molecules[1]. Similar issues apply for direct photochemistry, which is the direct phototransformation of water pollutants upon sunlight absorption.

Hydrology and chemistry of freshwaters affect PPRIs concentrations: $HO^{\bullet}$ and $CO_3^{\bullet-}$ photochemistry is favoured in shallow, DOM-poor waters, whilst the role of $^3$CDOM* and $^1O_2$ is more significant in deep, DOM-rich water bodies. In the context of climate change, hydrological drought events are expected to increase[2], and effects on freshwaters chemistry (and photochemistry) are thus expected[3]. This presentation addresses the consequences of hydrological drought and anthropogenic pollution on the photochemistry of Lower Lakes (Southern Australia) and rivers of Piedmont region (NW Italy)[4,5]. By means of photochemical modelling, the self-decontamination potential of these water bodies was assessed during drought events. The main findings showed that photochemical processes would be faster during drought and depend on the way by which water is lost.

(1) Vione and Carena, *Environ. Sci. Technol.* **2020**, *54*, 5328–5330. (2) Ukkola et al., *Geophys. Res. Lett.* **2020**, *46*, e2020GL087820. (3) Mosley, *Earth-Science Rev.* **2015**, *140*, 203–214. (4) Carena et al., *Chemosphere* **2021**, *263*, 127921. (5) Carena et al., *Chemosphere* **2019**, *236*, 124356.

**O 6**

# STABILITY AND TOXICITY OF UV FILTERS AND ITS TRANSFORMATION PRODUCTS UNDER DISINFECTION CONDITIONS

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Growing concern over deleterious effects of ultraviolet (UV) radiation on humans has caused an increased usage of sunscreen products with UV filter-containing formulations. UV filters are substances capable of absorbing, reflecting and/or scattering sunlight wavelengths, reducing the damage that this radiation might cause on human health. Although UV filters must be stable when exposed to UV light, under certain conditions they might decompose by light or may react with chlorine-based disinfection agents. The aim of this study is to investigate the transformation behaviour and toxicity changes of three benzophenone-type UV filters, diethylamino hydroxybenzoil hexyl benzoate (DHHB), 2-hydroxy-4-metoxybenzophenone (BP3) and 2-hydroxy-4-metoxybenzophenone-5-sulfonic acid (BP4) during chlorination disinfection treatment and under UV radiation. In reaction of NaOCl and DHHB 3-Cl DHHB was formed, and 3,5-diCl-DHHB in excess of disinfectant, and with BP3 and BP4 5-Cl-BP3 and 3,5-diClBP3 as a main product were formed. Photostability experiments showed that BP3, BP4 and DHHB UV filters and their mono-chlorinated by-products were stable under UV radiation, except 3,5-diCl BP3. Toxicity of chlorinated compounds tested by photobacteria *Vibrio fischeri* was found to be in the similar range as that of the starting compound. Microalgae were more sensitive to DHHB than to its chlorinated by-products, while daphnids were affected more by DHHB's chlorinated products. The comparative toxicity data showed DHHB and even more its chlorinated by-products as highly biologically potent to daphnids than another tested UV filter. Microalgae were similarly affected by DHHB and BP3, but BP4 has the lowest ecotoxicity.

**O 7**

# MICROALGAE-BASED REMOVAL OF CONTAMINANTS OF EMERGING CONCERN

Franja Prosenc[1,*], David Škufca[2], Ester Heath[2], Tjaša Griessler Bulc[1], Darja Istenič[1], Gianluigi Buttiglieri[3]

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Incomplete removals of contaminants of emerging concern (CECs) have been reported for conventional activated sludge (CAS) wastewater treatment technologies; however, information is still lacking for many CECs. The use of microalgae-based treatment systems such as high-rate algae ponds (HRAP) has gained significant interest over the past few years thanks to simultaneous removal capacity of organic and inorganic compounds and potentially CECs, as well as lower construction and operational cost as compared to CAS. In this study, a monoculture of *C. vulgaris* and mixed microalgal-bacterial culture are compared in terms of the removal of 28 CECs (bisphenols, substances from the 2018 EU Watch List, pharmaceuticals, and selected transformation products). The removal pathways were additionally followed in light and dark abiotic controls. Photobioreactors of 1 L volume were run at hydraulic retention times of 11-12 days and spiking CECs at environmentally relevant concentrations (1-20 µg $L^{-1}$). The results show that the mixed microalgal-bacterial culture was better at removing bisphenols as compared to a monoculture of *C. vulgaris*. Bisphenols' log $K_{ow}$ played a significant role in removal pathways, where bisphenols with high log $K_{ow}$ were removed abiotically while bisphenols with low log $K_{ow}$ were mainly biodegraded. The removal degree and the pathway of pharmaceuticals and EU Watch List substances were comparable between both cultures, showing no impact of log $K_{ow}$ for most compounds; however, the removal with *C. vulgaris* was faster for some compounds. The high log $K_{ow}$ caused the high removal of estradiol in abiotic controls showing the importance of adsorption onto biomass and suspended matter. Literature data show that microalgae-based treatment is at least as efficient, if not better than CAS.

**O 8**

# DETERMINATION OF THE AIR POLLUTION MARKERS IN MOSCOW SNOW USING GC-HRMS WITH COMPLEMENTARY IONIZATION TECHNIQUES

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Environmental exposure assessment is an important step in establishing a list of local priority pollutants and finding the sources of the threats. Exposome targeted and non-targeted analysis as well as suspect screening may be applied to reveal these pollutants. The non-targeted screening is a challenging task and requires the application of the most powerful available analytical tools, assuring wide analytical coverage, sensitivity, identification reliability, and quantitation.

Snow analysis represents an efficient approach for the estimation of long-term air pollution during winter period, due to accumulation and preservation of environmental contaminants by snow. Gas chromatography – high resolution time-of-flight mass spectrometry (GC-HR-TOFMS) with electron ionization (EI), positive chemical ionization (PCI), and electron capture negative ionization (ECNI) ion sources were used for the analysis of Moscow snow samples collected in the early spring of 2018 at nine different locations. The strategy of screening analysis combining GC-HRMS with complementary ionization techniques allowed expanding the list of target compounds by several hundred components belonging to various classes of pollutants. The large amount of information generated from results of targeted and non-targeted analysis makes appropriate application of different methods in big data analysis. This helps to observe the trends and tendencies in the pollution exposome across the city.

**O 9**

# THE PROBLEMATIC OF SILOXANES IN WWTPS AND BIOGAS PRODUCTION

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Volatile methyl siloxanes (VMSs) are a group of chemicals constituted by a methyl-saturated Si-O chain in linear or cyclic configuration. They are hydrophobic and present low viscosity, making them very appealing for their addition in cosmetics and personal care products as lubricants and surfactants. However, once they have been drained off through the grey water system, they end up in waste water treatment plants (WWTPs), where their behaviour is highly heterogeneous. The lighter and most volatile compounds leave these installations via aeration or effluent water, remaining in the environment enough time to reach distant locations and bioaccumulate. The heavier congeners partition to the sludge and subsequent biogas, compromising the use of this resource by corroding internal engine pieces after combustion. Therefore, specific strategies should be put in place to treat VMSs accordingly in WWTPs. Along this seminar it will be showed different methodologies to sample, extract, and analyse VMSs compounds in the matrixes present in WWTPs. Furthermore, a summary of the state-of-the-art technologies for siloxane removal and biogas purification will be displayed, in order to discuss the best approaches to face the mentioned drawbacks.

**O 10**

# DEVELOPMENT OF NOVEL MAGNETIC COMPOSITE $Fe_3O_4$/ PINE CONES GEL BEADS FOR HEAVY METALS REMOVAL IN SIMPLE AND BINARY SYSTEMS: EXPERIMENTAL AND THEORETICAL STUDIES

Manel Touihri[1],* Fatma Guesmi[1], Chiraz Hannachi[1], Béchir Hamrouni[1], Lotfi Sellaoui[2], Michael Badawi[3], Jordi Poch[4], Núria Fiol[5].

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The use of magnetic sorbents has gained a spread attention due to their eco-friendly characteristic, ease of separation and low cost. In this context, a novel biocomposite sorbent based on modified pine cone powder to obtain magnetic pine cone beads (MPCB) was developed and investigated for copper (II) and chromium (VI) removal in single and binary system. The structure and chemical properties of the prepared sorbent was characterized by SEM, EDX, FTIR and XRD analysis. Cu(II) and Cr(VI) optimal sorption conditions were established and the sorption mechanism was investigated; it mainly involved complexation/chelation with surface functional groups, electrostatic interaction and ion exchange. A physical model was adopted to attribute new physico-chemical interpretations of the adsorption mechanism. In the multi-components system, both competitive and synergistic effects were observed. The competitive sorption behavior of metal ions was analyzed by the modified competitive Langmuir model which provides good fit for the Cu experimental data. This study proves that the MPCB hold great promise for using as effective sorbent for heavy metals removal.

**O 11**

# METAL HOMEOSTASIS AND PHOTOSYNTHESIS IN SELECTED PLANTS

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Growing amount of metal nanoparticles being released to environment rises a fundamental question concerning heavy metals interactions with living organisms and fate. Metal based nanoparticles are a major group of nanospecies with production approaching one third of the global nano-market. They exhibit plethora of shapes and chemical compositions and tend to induce remarkable divergent effects on plants. Any reliable examination of the latter should take into consideration major environmental factors like, soil texture, temperature, pH, osmotic pressure, content and composition of organic matter, redox status of the soil environment, ionic strength, cation exchange capacity, mineral composition, interaction with others elements as present in the soil matrix and in root exudates. The uptake of heavy metals by roots occurs simultaneously with the physical and chemical reactions ongoing in rhizosphere and can influenced the nutrient absorption processes. The latter should be of a special importance when nanosized materials are being introduced to environment with either agrochemicals or substances used in soil or water remediation technologies. Despite numerous studies, the impact of nanoparticles on plants is not entirely recognized as yet. In particular, the problem of full comparability and transferability of experimental results is not to be neglected. Hydroponic cultivations which prompt accurate plant growth were applied in further studies. Phytotoxicity was estimated by fresh weights and photosynthesis parameters. Additionally Ce, Cu, Zn, Mn, Fe, Ca and Mg contents were analyzed by high-resolution continuum source atomic absorption and inductively coupled plasma optic emission spectrometries. Analysis of variance has proved that several nanoparticles affected metals uptake. For example, nanoparticulate $CeO_2$ reduced Cu, Zn, Mn, Fe, and Ca accumulation in pea shoots. The lowest Ce concentration boosted photosynthesis rate while remaining treatments did not induce significant changes.

**O 12**

# PILOT-SCALE PHOSPHORUS RECOVERY FROM WASTEWATER TO CREATE A SOIL IMPROVEMENT PRODUCT: AN ASSESSMENT OF ADSORBENT PERFORMANCE AND QUALITY

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Phosphorus (P) recovery from wastewater will become increasingly vital in the future as terrestrial rock phosphate deposits are expended. The Environmental Research Institute (ERI) has been developing the FILTRAFLO$^{TM}$-P reactor (with Veolia Water Technologies) to recover P from wastewater/septic tank effluent through a filtration/adsorption process (Phos4You Project - INTERREG VB North-West Europe). This small unit employs enhanced gravitational filtration through adsorption media (here, a novel KOH deacetylated crab carapace based chitosan-calcite adsorbent (CCM)) with continuous self-backwashing. The trials were designed to assess how the FILTRAFLO$^{TM}$-P unit would operate under 'real' conditions (low and high P levels), and to ascertain the effectiveness of the adsorbent to recover P from final effluent. A six-week trial of this technology was carried out at the Scottish Water Horizons Development Centre at Bo'ness in January-February 2020. High P recovery potential was achieved even at low P concentrations, bringing the residual effluent P level below 1 mg/L (EU limit for sensitive water bodies). Surface microprecipitation and inner-sphere complexation were postulated as the main P adsorption mechanisms due to reduced concentrations of Fe, Mn and Ca in wastewater. Further, the quality assessment of the P-enriched CCM was based on elemental composition (macro nutrients and heavy metals), microbiological evaluation and quantification of organic micropollutants. The quality analysis indicated ~3% $P_2O_5$, trace levels (well below legislative limits) of heavy metals (i.e., Cu, Co) and organic pollutants (e.g., PCBs) and no detectable levels of target bacterial pathogens. Future work will include pot (plant) growth trials to observe P uptake/availability levels in different soils.

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