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Environmental

Analysis of Semivolatile Organic Compounds in Drinking Water on the Agilent 8890 GC and 5977 GC/MSD with Extended Calibration Range

Angela Smith Henry, Ph.D.
Agilent Technologies, Inc, 2019

This application note coupled an Agilent 8890 GC with an Agilent 5977 MSD to analyze semivolatile organic compounds in drinking water sources according to United States Environmental Protection Agency (EPA) method 525. This workflow generated results that met method 525 calibration criteria, and demonstrated that this system is sufficiently sensitive to detect most of the low-level standards analyzed.

A Community Multi-Omics Approach towards the Assessment of Surface Water Quality in an Urban River System

David J. Beale, Avinash V. Karpe, Warish Ahmed, Stephen Cook, Paul D. Morrison, Christopher Staley, Michael J. Sadowsky, Enzo A. Palombo
International Journal of Environmental Research and Public Health, Volume 14, Issue 3, 303, 2017

A multi-omics approach was applied to an urban river system (the Brisbane River (BR), Queensland, Australia) in order to investigate surface water quality and characterize the bacterial population with respect to water contaminants. To do this, bacterial metagenomic amplicon-sequencing using Illumina next-generation sequencing (NGS) of the V5–V6 hypervariable regions of the 16S rRNA gene and untargeted community metabolomics using gas chromatography coupled with mass spectrometry (GC-MS) were utilized. The multi-omics data, in combination with fecal indicator bacteria (FIB) counts, trace metal concentrations (by inductively coupled plasma mass spectrometry (ICP-MS)) and *in-situ* water quality measurements collected from various locations along the BR, were then used to assess the health of the river ecosystem. Sites sampled represented the transition from less affected (upstream) to polluted (downstream) environments along the BR. Chemometric analysis of the combined datasets indicated a clear separation between the sampled environments. *Burkholderiales* and *Cyanobacteria* were common key factors for differentiation of pristine waters. Increased sugar alcohol and short-chain fatty acid production was observed by *Actinomycetales and Rhodospirillaceae* that are known to form biofilms in urban polluted and brackish waters. Results from this study indicate that a multi-omics approach enables a deep understanding of the health of an aquatic ecosystem, providing insight into the bacterial diversity present and the metabolic output of the population when exposed to environmental contaminants.

Comparison of pyrolysis gas chromatography/mass spectrometry and hyperspectral FTIR imaging spectroscopy for the analysis of microplastics

Sebastian Primpke, Marten Fischer, Claudia, Lorenz, Gunnar Gerdts, and Barbara M. Scholz- Böttcher
Analytical and Bioanalytical Chemistry, 412, 8283–8298, 2020

Analysis of microplastics (MP) in environmental samples is an emerging field, which is performed with various methods and instruments based either on spectroscopy or thermoanalytical methods. In general, both approaches result in two different types of data sets that are either mass or particle number related. Depending on detection limits of the respective method and instrumentation the derived polymer composition trends may vary. In this study, we compare the results of hyperspectral Fourier-transform infrared (FTIR) imaging analysis and pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) analysis performed on a set of environmental samples that differ in complexity and degree of microplastic contamination. The measurements were conducted consecutively, and on exactly the same sample. First, the samples were investigated with FTIR using aluminum oxide filters; subsequently, these were crushed, transferred to glass fiber filters, in pyrolysis cups, and measured via Py-GC/MS. After a general data harmonization step, the trends in MP contamination were thoroughly investigated with regard to the respective sample set and the derived polymer compositions. While the overall trends in MP contamination were very similar, differences were observed in the polymer compositions. Furthermore, polymer masses were empirically calculated from FTIR data and compared with the Py-GC/MS results. Here, a most plausible shape-related overestimation of the calculated polymer masses was observed in samples with larger particles and increased particle numbers. Taking into account the different measurement principles of both methods, all results were examined and discussed, and future needs for harmonization of intermethodological results were identified and highlighted.

Detection of methoxylated and hydroxylated polychlorinated biphenyls in sewage sludge in China with evidence for their microbial transformation

Jianteng Sun, Lizhong Zhu, Lili Pan, Zi Wei, Yao Song, Yuduo Zhang, Liping Qu, Yu Zhan
Scientific Reports, Volume 6, Issue 1, 2016

The concentrations of methoxylated polychlorinated biphenyls (MeO-PCBs) and hydroxylated polychlorinated biphenyls (OH-PCBs) were measured in the sewage sludge samples collected from twelve wastewater treatment plants in China. Two MeO-PCB congeners, including 3'-MeO-CB-65 and 4'-MeO-CB-101, were detected in three sludge with mean concentrations of 0.58 and 0.52 ng/g dry weight, respectively. OH-PCBs were detected in eight sludge samples, with an average total concentration of 4.2 ng/g dry weight. Furthermore, laboratory exposure was conducted to determine the possible source of OH-PCBs and MeO-PCBs in the sewage sludge, and their metabolism by the microbes. Both 4'-OH-CB-101 and 4'-MeO-CB-101 were detected as metabolites of CB-101 at a limited conversion rate after 5 days. Importantly, microbial interconversion between OH-PCBs and MeO-PCBs was observed in sewage sludge. Demethylation of MeO-PCBs was favored over methylation of OH-PCBs. The abundant and diverse microbes in sludge play a key role in the transformation processes of the PCB analogues. To our knowledge, this is the first report on MeO-PCBs in environmental matrices and on OH-PCBs in sewage sludge. The findings are important to understand the environmental fate of PCBs.

The effects of humidity and ammonia on the chemical composition of secondary aerosols from toluene/NOx photo-oxidation

Linghong Chen, Zhier Bao, Xuecheng Wu, Kangwei Li, Lixia Han, Xingya Zhao, Xin Zhang, Zhihua Wang, Merched Azzi, Kefa Cen
The Science of the Total Environment, Volume 728, 2020

The secondary aerosol formation mechanism in the presence of ammonia (NH_3), is poorly understood, especially under high relative humidity (RH) conditions. In this study, a total of seven experiments were conducted from toluene/NOx photo-oxidation in the presence/absence of NH_3 under dry (~7% RH) and wet (>60% RH) conditions in a ~3 m^3 smog chamber. A series of instruments including gas analysers, scanning mobility particle sizer (SMPS), aerosol mass spectrometry (HR-ToF-AMS) etc. were applied to measure the NOx and O_3 concentrations, the mass concentration and chemical composition of secondary aerosol. It was found that NH_3 could enhance the mass loading of secondary aerosol, especially under wet condition. However, the presence of NH_3 or increasing RH did not have a significant influence on SOA yield. The organic aerosol mass spectrum from AMS showed that the most abundant fragment was at *m/z* = 44, which was mainly from the fragmentation of carboxylic acids. Compared to the absence of NH_3, the fraction of fragment at *m/z* = 44 and O:C was higher in the presence of NH_3, regardless of dry or wet conditions. The highest O:C value of 0.71–0.75 was observed in the presence of NH_3 under wet condition, suggesting there could be a synergetic effect between the high RH and the presence of NH_3, which jointly contributed to the photochemical aging process of SOA. The N:C increased in the presence of NH_3 under both dry and wet conditions, which might be attributed to the carboxylates and organic nitrates formed from the reaction between NH_3 and carboxylic acids. The results implied that SOA modelling should consider the role of NH_3 and water vapour, which might fill the gap of O:C between laboratory studies and field measurements.

Electrochemical/Peroxymonosulfate/NrGO-$MnFe_2O_4$ for Advanced Treatment of Landfill Leachate Nanofiltration Concentrate

Zhengguang He, Manjing Lu, Jiaqi Wang, Yuzhong Wang
Water, 13(4), 413, 2021

A simple one-pot method was used to successfully embed manganese ferrite ($MnFe_2O_4$) nanoparticles on the nitrogen-doped reduced graphene oxide matrix (NrGO), which was used to activate peroxymonosulfate to treat the landfill leachate nanofiltration concentration (LLNC) with electrochemical enhancement. NrGO-$MnFe_2O_4$ and rGO-$MnFe_2O_4$ were characterized by various means. This indicates that nitrogen-doped could induce more graphene oxide (GO) spall and reduction to produce more active centers, and was favorable for uniformly loading $MnFe_2O_4$ particles. The comparison between electrochemical/peroxymonosulfate/NrGO-$MnFe_2O_4$ (EC/PMS/NrGO-$MnFe_2O_4$) system and different catalytic systems shows that electrochemical reaction, NrGO and $MnFe_2O_4$ can produce synergies, and the chemical oxygen demand (COD) removal rate of LLNC can reach 72.89% under the optimal conditions. The three-dimensional (3D-EEM) fluorescence spectrum shows that the system has a strong treatment effect on the macromolecules with intense fluorescence emission in LLNC, such as humic acid, and degrades into substances with weak or no fluorescence characteristics. Gas chromatography-mass spectrometry (GC-MS) indicates that the complex structure of refractory organic compounds can be simplified, while the simple small molecular organic compounds can be directly mineralized. The mechanism of catalytic degradation of the system was preliminarily discussed by the free radical quenching experiment. Therefore, the EC/PMS/NrGO-$MnFe_2O_4$ system has significant application potential in the treatment of refractory wastewater.

Emerging and legacy per- and polyfluoroalkyl substances in water, sediment, and air of the Bohai Sea and its surrounding rivers

Zhen Zhao, Xianghui Cheng, Xia Hua, Bin Jiang, Chongguo Tian, Jianhui Tang, Qilu Li, Hongwen Sun, Tian Lin, Yuhong Liao, Gan Zhang
Environmental Pollution, Volume 263, Part A, 2020

Per- and polyfluoroalkyl substances (PFASs) contamination in the Bohai Sea and its surrounding rivers has attracted considerable attention in recent years. However, few studies have been conducted regarding the distribution of PFASs in multiple environmental media and their distributions between the suspended particles and dissolved phases. In this study, surface water, surface sediment, and air samples were collected at the Bohai Sea to investigate the concentration and distribution of 39 targeted PFASs. Moreover, river water samples from 35 river estuaries were collected to estimate PFAS discharge fluxes to the Bohai Sea. The results showed that total ionic compound (Σi-PFASs) concentrations ranged from 19.3 to 967 ng/L (mean 125 ± 152 ng/L) in the water and 0.70–4.13 ng/g dw (1.78 ± 0.76 ng/g) in surface sediment of the Bohai Sea, respectively. In the estuaries, Σi-PFAS concentrations were ranged from 10.5 to 13500 ng/L (882 ± 2410 ng/L). In the air, ΣPFAS (Σi-PFASs + Σn-PFASs) concentrations ranged from 199 to 678 pg/m^3 (462 ± 166 pg/m^3). Perfluorooctanoic acid (PFOA) was the predominant compound in the seawater, sediment, and river water; in the air, 8:2 fluorotelomer alcohol was predominant. Xiaoqing River discharged the largest Σi-PFAS flux to the Bohai Sea, which was estimated as 12,100 kg/y. Some alternatives, i.e., 6:2 fluorotelomer sulfonate acid (6:2 FTSA), hexafluoropropylene oxide dimer acid (HFPO-DA), and chlorinated 6:2 polyfluorinated ether sulfonic acid (Cl-6:2 PFESA), showed higher levels than or comparable concentrations to those of the C8 legacy PFASs in some sampling sites. The particle-derived distribution coefficient in seawater was higher than that in the river water. Using high resolution mass spectrometry, 29 nontarget emerging PFASs were found in 3 river water and 3 seawater samples. Further studies should be conducted to clarify the sources and ecotoxicological effects of these emerging PFASs in the Bohai Sea area.

Enhanced treatment of dispersed dye-production wastewater by self-assembled organobentonite in a one-step process with poly-aluminium chloride

Lizhong Zhu, Yao Liu
Scientific Reports, Volume 7, Issue 1, 2017

Organobentonite has been successfully applied in industrial wastewater treatment. However, the solid-liquid separation in wastewater treatment still needs improvement. This study presents an enhanced approach with high removal efficiency and short separation time for dispersed dye-production wastewater using self-assembled organobentonite in a one-step process with poly-aluminium chloride (PAC). The enhanced effects of PAC on wastewater treatment by organobentonite were comprehensively evaluated. Following the primary decontamination by the self-assembled organobentonite, the removal efficiency for dispersed dye-production wastewater was strengthened with PAC coagulation. The removal rates of TOC and organic pollutants were 55.0% and 63.5%, respectively, with the PAC-enhanced approach and were 1.3- and 1.6-fold higher, respectively, than those with the self-assembled organobentonite approach. The combination of PAC with self-assembled organobentonite was able to break the stability of the organobentonite suspension and enlarge the floc size, and thus reduce the solid-liquid separation time from 30 min to 10 min. Additionally, this enhanced approach could improve the biodegradability of wastewater with the BOD_5/COD_{Cr} ratio increasing from 0.22 to 0.39, which was 4.1-fold higher than that of only organobentonite in a one-step process. Therefore, the PAC-enhanced approach could be a promising technology for wastewater pretreatment in practical industrial applications.

EPA 8270E with Pulsed Split Injection and Retention Time Locking on an 8890 GC with a 5977 Series MSD

Rachael Ciotti

Agilent Technologies, Inc, 2020

United States Environmental Protection Agency (US EPA) Method 8270 provides conditions for analyzing more than 200 semivolatile organic compounds (SVOCs) by gas chromatography/mass spectrometry (GC/MS). This Application Note demonstrates system optimization, calibration, and method performance for the recently revised EPA 8270E on an Agilent 8890 GC system coupled with an Agilent 5977 Series single quadrupole mass spectrometer. It uses a pulsed split injection and a 9 mm extractor lens to enable rapid sample transfer and a wide dynamic range. Agilent's unique retention time locking (RTL) feature was used for ease-of-identification following maintenance. Finally, a DFTPP tune evaluation in accordance with updated tune criteria in EPA Method 8270E is also discussed.

Holocene Interactions Between Glacier Retreat, Sea Ice Formation, and Atlantic Water Advection at the Inner Northeast Greenland Continental Shelf

Nicole Syring, Jeremy M. Lloyd, Ruediger Stein, Kirsten Fahl, Dave H. Roberts, Louise Callard, Colm O'Cofaigh

Paleoceanography and Paleoclimatology, Volume 35, Issue 11, 2020

During the past four decades significant decrease in Arctic sea ice and a dramatic ice mass loss of the Greenland Ice Sheet (GIS) has been coincident with global warming and an increase in atmospheric CO2. In Northeast Greenland significant mass loss from the outlet glaciers Nioghalvfjerdsbræ (79NG) and Zachariæ Isstrøm (ZI) and intensive seasonal breakup of the local Norske Øer Ice Barrier (NØIB) have also been observed since 2000. In order to better understand the processes driving these modern changes, studies of paleoclimate records are important and of major societal relevance. A multiproxy study including organic-biogeochemical and micropaleontological proxies was carried out on a marine sediment core recovered directly in front of 79NG. Data from Core PS100/270 evidenced a strong inflow of warm recirculating Atlantic Water across the Northeast Greenland shelf from the early Holocene between ~10 and 7.5 ka. An overall high in phytoplankton productivity occurred within a stable sea ice margin regime, accompanied by 79NG retreat most probably triggered by peak solar insolation and changes in the local ocean circulation. Enhanced basal melt of the underside of 79NG at ~7.5 ka then led to the total disintegration of the ice shelf. The released freshwater would have driven water column stratification and promoted the formation of the local landfast ice barrier, which is shown by lowered biomarker values and foraminifera abundances toward the end of the early Holocene. Near perennial sea ice conditions with short summers and 79NG retreat to the inner fjord then prevailed from ~7.5 to ~0.8 ka.

Microplastic Mass Concentrations and Distribution in German Bight Waters by Pyrolysis-Gas Chromatography-Mass Spectrometry/Thermochemolysis Reveal Potential Impact of Marine Coatings: Do Ships Leave Skid Marks?

Christopher Dibke, Marten Fischer, Barbara M. Scholz-Boettcher
Environmental Science & Technology, 55, 4, 2285-2295, 2021

In this first mass-related survey of microplastics (MPs, <1 mm) in the German Bight (North Sea, 2.5 m water depth), spatial load, temporal variations, and potential sources were examined. Relevant plastic types were detected using pyrolysis–gas chromatography–mass spectrometry/thermochemolysis (Py-GC/MS). This suitable method provides qualitative and trace-level polymer or polymer cluster-specific mass quantitative MP data. Neither MP concentration (2–1396 µg m^{-3}) nor type distribution was homogeneous. Concentrations appeared to be substantially influenced by meteorological and oceanographic conditions. The coastal MP-type composition showed an overprint indicating a packaging waste-related signal. Considerably different compositions were observed in central and estuarine areas. Here, a close relation to marine (antifouling) coating particles, i.e., abrased chlorinated rubber-, acryl-styrene-, and epoxide binder-containing particles are hypothesized as the main MP source, indicating ship "skid marks". They represent a dominant, toxicologically relevant but underestimated marine-based MP share, inverting the widely cited 80% terrestrial- to 20% marine-based debris ratio for MPs. In consequence of the findings, polymer clusters attributed to the basic polymers polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate), poly(vinyl chloride), poly(methyl methacrylate), and polycarbonate are proposed for Py-GC/MS MPs mass determination based on specific thermal decomposition products linked to related polymer structural units.

Occurrence and removal of organic pollutants by a combined analysis using GC-MS with spectral analysis and acute toxicity

Qiong Liu, Zhe Zhao, Hui Li, Ming Su, Shu-xuan Liang
Ecotoxicology and Environmental Safety, Volume 207, 2021

The presence of xenobiotic compounds especially organic micro-pollutants in municipal wastewater treatment plant (MWWTP) is a major concern worldwide. The occurrence and removal of trace organic pollutants in a MWWTP by a combined analysis using GC-MS with spectral analysis and acute toxicity were studied in this work. Non-target screening and toxicity analysis of organic compounds were conducted to understand the types of toxic and refractory pollutants in municipal wastewater and evaluated the toxicity removal efficiency of MWWTP. The results showed that most of the effects were significantly reduced or completely eliminated during the wastewater treatment process, while some compounds, such as antioxidants, drugs, and organic plasticizers, had detection rates of up to 100% at each site, indicating that these harmful substances remained throughout wastewater treatment process. Based on Pearson correlation analysis, paired correlation analysis showed a positive correlation between UV_{254}, humification index, conventional parameters, and organic acute toxicity, while acute toxicity was negatively correlated with biological index and fluorescence index. The results indicated that the composition of MWWTP had a similar influence law in different locations, and the combination of spectral analysis provided a new insight to qualitatively and quantitatively showed the distribution of organic pollutants in the wastewater treatment system.

Optimized GC/MS Analysis for PAHs in Challenging Matrices

Anastasia A. Andrianova, Bruce D. Quimby
Agilent Technologies, Inc, 2019

The Agilent 8890 GC combined with an Agilent 5977 Series MSD system was used for the analysis of polycyclic aromatic hydrocarbons (PAHs). By proper selection of instrument configuration and operating conditions, the system provides a robust means of analyzing PAHs in difficult matrices. Midcolumn backflushing, continuous hydrogen source cleaning (JetClean), and use of an alternative drawout lens result in excellent linearity across a calibration range of 1 to 1,000 pg. System precision and robustness are demonstrated with replicate injections of an extract from high organic content soil.

Rapid Screening Workflow for Phthalates in Plastics by GC/MSD in Under Six Minutes

Anastasia A. Andrianova, Bruce D. Quimby
Agilent Technologies, Inc, 2020

The Agilent Intuvo 9000/5977B GC/MSD system provides a fast screening workflow for the qualitative detection of phthalates in plastics. This method used a GC oven with direct heating technology and MS spectral deconvolution. Phthalates were extracted from two real-world plastic samples by immersing a cut piece in acetone for 30 seconds. The extract was then injected onto the GC/MSD system. The direct heating oven allowed a high-temperature program rate of 250 °C/min, enabling the completion of the GC/MS analysis in 3.4 minutes. Spectral deconvolution was coupled with the library search algorithm and time-filtering using retention indices. This workflow provided rapid identification of phthalates present in the plastic. The user-created library of pesticides and environmental pollutants and the NIST 17 spectral library were used for compound identification. The entire analysis from sample collection to reporting took under six minutes. This approach is particularly useful for prioritizing samples for more in-depth analysis.

Reducing Analysis Time of 8270D with the Intuvo 9000 GC

Matthew Giardina, Mark Johnston, Bruce D. Quimby, Anastasia Andrianova
Agilent Technologies, Inc, Test America, Inc, 2018

Requirements and methods for the quantitation of semivolatile organic compounds (SVOCs) are described in method 8270D produced by the Environmental Protection Agency (EPA). This Application Note presents GC method translation from one developed for EPA 8270D, using a 30 m × 0.25 mm column, to a faster method using a conductively heated 20 m × 0.18 mm column on an Agilent Intuvo 9000 GC.

Systematic Development of a Simultaneous Determination of Plastic Particle Identity and Adsorbed Organic Compounds by Thermodesorption-Pyrolysis GC/MS (TD-Pyr-GC/MS)

Thomas Letzel, Jörg E. Drewes, Johanna Graßmann, Julia Reichel
Molecules, October 2020, 25(21): 4985

Micro-, submicro- and nanoplastic particles are increasingly regarded as vectors for trace organic chemicals. In order to determine adsorbed trace organic chemicals on polymers, it has usually been necessary to carry out complex extraction steps. With the help of a newly designed thermal desorption pyrolysis gas chromatography mass spectrometry (TD-Pyr-GC/MS) method, it is possible to identify adsorbed trace organic chemicals on micro-, submicro- and nanoparticles as well as the particle short chain polymers in one analytical setup without any transfers. This ensures a high sample throughput for the qualitative analysis of trace substances and polymer type. Since the measuring time per sample is only 2 h, a high sample throughput is possible. It is one of the few analytical methods which can be used also for the investigation of nanoplastic particles. Initially adsorbed substances are desorbed from the particle by thermal desorption (TD); subsequently, the polymer is fragmented by pyrolysis (PYR). Both particle treatment techniques are directly coupled with the same GC-MS system analyzing desorbed molecules and pyrolysis products, respectively. In this study, we developed a systematic and optimized method for this application. For method development, the trace organic chemicals phenanthrene, α-cypermethrin and triclosan were tested on reference polymers polystyrene (PS), polymethyl methacrylate (PMMA) and polyethylene (PE). Well-defined particle fractions were used, including polystyrene (sub)micro- (41 and 40 µm) and nanoparticles (78 nm) as well as 48-µm sized PE and PMMA particles, respectively. The sorption of phenanthrene (PMMA << PS 40 µm < 41 µm < PE < PS 78 nm) and α-cypermethrin (PS 41 µm < PS 40 µm < PE < PMMA < PS 78 nm) to the particles was strongly polymer-dependent. Triclosan adsorbed only on PE and on the nanoparticles of PS (PE < PS78).

A three-phase-successive partition-limited model to predict plant accumulation of organic contaminants from soils treated with surfactants

Zhiheng Li, Wei Wang, Lizhong Zhu
Environmental Pollution, June 2020, 261:114071

The application of surfactants is an effective way to inhibit the migration of organic contaminants (OCs) from soil to plants, and thus would be a great candidate method for producing safe agricultural products in organic-contaminated farmland. In this study, it was found that cetyltrimethyl ammonium bromide (CTMAB) reduced the OCs in cabbage by 22.0-64.1%, and those in lettuce by 18.8-36.5%. We developed a mathematical model to predict the accumulation of OCs in plants in the presence of surfactants. The successive partitioning of OCs among three phases, namely, soil, soil water and plant roots, was considered. The equilibrium of OC between the soil and soil water was scaled using the sorption coefficient of OCs on soils normalized by the soil organic carbon (K_{oc}) and carbon-normalized OCs sorption coefficient with the sorbed surfactants (K_{ss}). To precisely calculate the K_{oc} and K_{ss}, the bioavailable and bound OCs were measured using a sequential extraction method. Linear positive correlations between the logarithm of K_{oc} (or K_{ss}) and the logarithm of the octanol-water partition coefficient (log K_{ow}) of OCs were established for laterite soils, paddy soils and black soils. In the presence of CTMAB, the equilibrium of OCs between the soil water and plant roots was scaled using the carbon-normalized OC sorption coefficient with the sorbed surfactants (K_{sf}), whose logarithmic value was linearly correlated with the log K_{ow} of the OCs. A three-phase-successive partition-limited model was developed based on these relationships, demonstrating an average prediction accuracy of 76.6 ± 36.8%. Our results indicated that the decrease in bioavailable OCs in soils and the increase in sorption of OCs on roots should be taken into consideration when predicting plant uptake. This research provides a validated mathematical model for predicting the concentration of OCs in plants in the presence of surfactants.

Trace determination of eleven natural estrogens and insights from their occurrence in a municipal wastewater treatment plant and river water

Yu Liu, Zhao Tang, Ze-Hua Liu, Hao Wang, Zhi Dang, Yin Hua, Yan Zhou, Yu Liu
Water Research, September 2020, 182:115976

As endocrine disruptors, natural estrogens including estrone (E1), 17β-estradiol (E2), and estriol (E3) in wastewaters of municipal wastewater treatment plant (WWTP) as well as other environmental matrix have been widely studied. However, the far-less studied natural estrogens such as 2-hydroxyestrone (2OHE1), 16α-hydroxyestrone (16α-OHE1), 4-hydroxyestrone (4OHE1), etc., found in human urine have been almost ignored. Therefore, it is important to investigate the occurrence of these far-less studied natural estrogens in municipal WWTP and other environment. In this study, a GC-MS analytical method was firstly established and validated for trace determination of eleven natural estrogens in waste and surface waters, including E1, E2, E3, 2OHE1, 16α-OHE1, 4OHE1, 2-hydroxyestradiol (2OHE2), 4-hydroxyestradiol (4OHE2), 17-epiestriol (17epiE3), 16-epiestriol (16epiE3), and 16keto-estradiol (16ketoE2). All the eleven natural estrogens were detected in the influent of one municipal WWTP, which ranged from 7.9 to 62.9 ng/L. The top five natural estrogens in the influent were E1, E3, 16α-OHE1, 16ketoE2, and 2OHE1 with respective concentrations of 62.9, 62.6, 46.9, 32.7, and 28.8 ng/L. Most of them were detected in both the effluent and river water, in which their detected concentrations were n.d-14.7 and n.d-51.7 ng/L, respectively. This work is the first to indicate that the so far less commonly studied natural estrogens in the environment likely pose adverse health effect on humans and wildlife due to their relative strong estrogenic potencies and high levels in wastewater and river water. More work should be done to understand their removals in municipal WWTPs and their occurrence in surface waters.

US EPA Method 524.2: Successful Measurement of Purgeable Organic Compounds in Drinking Water by Agilent 8860/5977B GC/MSD

Bruce D. Quimby, Anastasia A. Andrianova
Agilent Technologies, Inc, 2019

An Agilent 8860/5977B GC/MSD system coupled with a Teledyne Tekmar Lumin purge and trap (P&T) concentrator and an AQUATek liquid vial autosampler (LVA) was successfully used for the analysis of volatile organic compounds (VOCs) to the requirements of United States Environmental Protection Agency (US EPA) method 524.2. The analysis of VOCs in water following this or similar methods are widely used around the world as part of insuring the safety of potable water supplies.

Valorizing Plastic-Contaminated Waste Streams through the Catalytic Hydrothermal Processing of Polypropylene with Lignocellulose

Sukanya Hongthong, Hannah S. Leese, Christopher J. Chuck
ACS Omega, 2020, 5(32), 20586-20598

Food waste is a promising resource for the production of fuels and chemicals. However, increasing plastic contamination has a large impact on the efficiency of conversion for the more established biological routes such as anaerobic digestion or fermentation. Here, we assessed a novel route through the hydrothermal liquefaction (HTL) of a model waste (pistachio hulls) and polypropylene (PP). Pure pistachio hulls gave a biocrude yield of 34% (w/w), though this reduced to 16% (w/w) on the addition of 50% PP in the mixture. The crude composition was a complex blend of phenolics, alkanes, carboxylic acids, and other oxygenates, which did not change substantially on the addition of PP. Pure PP does not breakdown at all under HTL conditions (350 °C, 15% solids loading), and even with biomass, there is only a small synergistic effect resulting in a conversion of 19% PP. This conversion was enhanced through using typical HTL catalysts including Fe, $FeSO_4{\cdot}7H_2O$, $MgSO_4{\cdot}H_2O$, $ZnSO_4{\cdot}7H_2O$, ZSM-5, aluminosilicate, Y-zeolite, and Na_2CO_3; the conversion of PP reached a maximum of 38% with the aluminosilicate, for example. However, the PP almost exclusively broke down into a solid-phase product, with no enhancement of the biocrude fraction. The mechanism was explored, and with the addition of the radical scavenger butylated hydroxytoluene (BHT), the conversion of plastic reduced substantially, demonstrating that radical formation is necessary. As a result, the plastic conversion was enhanced to over 50% through the addition of the co-solvent and hydrogen donor, formic acid, and the radical donor, hydrogen peroxide. The addition of formic acid also changed the crude composition, including more carboxylic acids and oxygenated species than the conversion of the biomass alone; however, the majority of the carbon distributed to the volatile organic gas fraction producing an array of short-chain volatile hydrocarbons, which potentially could be repolymerized as a polyolefin or combined with the biocrude for further processing. Catalytic HTL was therefore shown to be a promising method for the valorization of polyolefins with biomass under typical HTL conditions.

Food

Aromatic Characterization of Mangoes (L.) Using Solid Phase Extraction Coupled with Gas Chromatography-Mass Spectrometry and Olfactometry and Sensory Analyses

Haocheng Liu, Kejing An, Siqi Su, Yuanshan Yu, Jijun Wu, Gengsheng Xiao, Yujuan Xu
Foods, January 2020, 9(1): 75

Mangoes (*Mangifera indica L.*) are wildly cultivated in China with different commercial varieties; however, characterization of their aromatic profiles is limited. To better understand the aromatic compounds in different mango fruits, the characteristic aromatic components of five Chinese mango varieties were investigated using headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography-mass spectrometry-gas chromatography-olfactometry (GC-MS-O) techniques. Five major types of substances, including alcohols, terpenes, esters, aldehydes, and ketones were detected. GC-O (frequency detection (FD)/order-specific magnitude estimation (OSME)) analysis identified 23, 20, 20, 24, and 24 kinds of aromatic components in Jinmang, Qingmang, Guifei, Hongyu, and Tainong, respectively. Moreover, 11, 9, 9, 8, and 17 substances with odor activity values (OAVs) ≥1 were observed in Jinmang, Qingmang, Guifei, Hongyu, and Tainong, respectively. Further sensory analysis revealed that the OAV and GC-O (FD/OSME) methods were coincided with the main sensory aromatic profiles (fruit, sweet, flower, and rosin aromas) of the five mango pulps. Approximately 29 (FD ≥ 6, OSME ≥ 2, OAV ≥ 1) aroma-active compounds were identified in the pulps of five mango varieties, namely, γ-terpinene, 1-hexanol, hexanal, terpinolene trans-2-heptenal, and *p*-cymene, which were responsible for their special flavor. Aldehydes and terpenes play a vital role in the special flavor of mango, and those in Tainong were significantly higher than in the other four varieties.

Characterization of key odor-active compounds in commercial high-salt liquid-state soy sauce by switchable GC/GC x GC-olfactometry-MS and sensory evaluation

Xiaojun Wang, Mengyao Guo, Huanlu Song, Qi Meng, Xiaosheng Guan
Food Chemistry, Volume 342, 2021

Activity of odor compounds of soy sauces has not been fully determined so far. Herein, a new switchable GC/GC × GC–olfactometry–mass spectrometry system for simultaneous GC × GC–MS analysis and sniffing of each odor-active substance through a single injection was used for the aroma extract dilution analysis of five regular high-salt liquid-state soy sauces (HLS). Methional, maltol, guaiacol, 4-ethylguaiacol, 2-acetylpyrrole, 2-acetylfuran, 2-phenylethanol, and 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone showed high flavor dilution (FD) factors. The FD factors of all odor-active compounds in different odor attributes were summed up (score) to evaluate the odor characteristics of the samples. Cooked potato-like odor was the most important characteristic. The difference in the odor characteristics were mainly reflected in the balance of caramel-like/sweet, roasted/roasted nut-like, spicy/burnt, and unpleasant odor intensity; the fruity odor intensity was the weakest. This study will provide a better understanding of the odor characteristics and key odor-active compounds in Chinese regular commercial HLS.

Chemical and Physical Implications of the Use of Alternative Vessels to Oak Barrels during the Production of White Wines

Mariona Gil I Cortiella, Cristina Ubeda, Jose Ignacio Covarrubias, V. Felipe Laurie, Alvaro Penan-Neira
Molecules, January 2021, 26(3): 554

Recently, the use of alternative vessels to oak barrels during winemaking has become increasingly popular, but little is known about their impact on the chemical composition of the resulting wines. To address this issue, a Sauvignon Blanc wine was elaborated from the same grape juice by using cylindrical stainless-steel tanks, oval-shaped concrete vessels, oval-shaped polyethylene vessels, and clay jars in triplicate. Each vessel was used for alcoholic fermentation and the aging of wines over its own lees. Wines elaborated in concrete vessels showed the highest pH and the lowest titratable acidity, most likely related to the observed release of inorganic compounds from the concrete walls. Little effect of the vessels was seen on the wine color and phenolic composition. Wines elaborated in clay jars showed the highest turbidity and the highest content of soluble polysaccharides, while those made using cylindrical stainless-steel tanks showed the highest content of volatile compounds. Despite the observed differences, all of the vessels tested seem suitable for white wine production since every wine showed chemical features that corresponded with the quality standards of Sauvignon Blanc wines.

Chemical constituents, antibacterial and antioxidant properties of the essential oil flower of *Tagetes minuta* grown in Cala community Eastern Cape, South Africa

Aboi Igwaran, Benson Chucks Iweriebor, Sunday Ofuzim Okoh, Uchechukwu Uchechukwu Nwodo, Larry Chikwelu Obi, Anthony Ifeanyi Okoh
BMC Complementary and Alternative Medicine, Volume 17, Issue 1, 2017

Background. *Tagetes minuta* has a long record of human use for the treatment of stomach and intestinal diseases. Most drugs used for diseases treatment are less efficacious with side effects and this brought the search for new treatment regimens mainly from medicinal plants.

Method. The essential oil (EO) was extracted by Clevenger's-type apparatus and its chemical composition, antioxidant and antibacterial properties were determined by GC-MS, spectrophotometric and broth dilution methods respectively. *S. uberis*, *E. cloacae, S. aureus, M. smegmatis, L. ivanovii, Vibrio* spp. and *E. coli* bacteria strains were used as test bacteria.

Results. GC-MS analysis revealed 98 compounds in the EO flower of *T. minuta* and β-Ocimene (14. 40%) was the major chemical constituents. The EO exhibited highest inhibitory effect against DPPH radical, followed by its effect on ABTS, while LP radical showed the least sensitivity with IC50 values of 2.45 mg/mL, 2.76 mg/mL and 3.23 mg/mL respectively. The EO showed antibacterial activities against all test organisms with MIC value for *S. aureus, M. smegatis* and *S. uberis* at 0.125 mg/mL and for L. ivanovii, *Vibrio* spp., *E. cloacae* and *E. coli* at 0.06 mg/mL. The EO showed MBC against E. cloacae and *E. coli* at 0.06 mg/mL, at 0.5 mg/mL for *S. uberis* and 0.125 mg/mL for *Vibrio* spp.

Conclusion. Findings from this study suggest that the EO of *T. minuta* flower may be a useful candidate in the search for lead constituents for the synthesis of new potent antibacterial and antioxidant agent.

Effect of solid-state fungal fermentation on the non-volatiles content and volatiles composition of *Coffea canephora* (Robusta) coffee beans

Vivien Chia Yen Tang, Jingcan Sun, Maurin Cornuz, Bin Yu, Benjamin Lassabliere
Food Chemistry, Volume 337, 2021

In this study, the effects of fungal fermentation on green canephora coffee beans were evaluated by observing the changes to selected non-volatile parameters before roasting, and subsequently the volatile profile after roasting. Solid-state fermentation (SSF) by *Aspergillus* spp. and *Mucor* spp. on green canephora coffee beans was shown to modulate the contents of free sugars, free amino acids and polyphenolic compounds such as caffeoylquinic acids (CQAs). Significant strain-specific differences were observed in the contents of aroma compounds after roasting. A significant increase in pyrazines was observed in the *Aspergillus oryzae*-fermented samples, while higher levels of furans were detected in the *Mucor plumbeus*-fermented samples. The present work shows that fungal fermentation of green canephora coffee beans is a potentially promising method for the modulation and improvement of coffee flavour and aroma.

Extraction optimization and microencapsulation of phenolic antioxidant compounds from lemon balm (*Melissa officinalis* L.): Instant soluble tea production

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Journal of Food Processing and Preservation, 2021, 45: e14995

The purpose of this study was to extract phenolics from lemon balm followed by microencapsulation with spray drying. The optimum extraction conditions were 100°C for the temperature and 120 min for the time with TPC of 6,365 mg GAE/100 g and ABTS radical scavenging activity of 9,196 mg TEAC/100 g. Lemon balm extracts were spray dried using three different air inlet temperatures (130°C, 165°C, and 200°C) of which 165°C was provided better scores than the other points in terms of microencapsulation yield (65.9%), microencapsulation efficiency (99.4%), dry matter (98.3%), and water activity (0.160). The inlet air temperatures had an insignificant ($p > .05$) effect on the antioxidant capacity of the microcapsules. Phenolic acids in lemon balm were slightly affected by the extraction and spray drying conditions. However, extraction followed by spray drying resulted in significant loss in the amount of volatiles such as geranial, neral, citronellal, and caryophyllene. Hot water extracts of the medicinal and aromatic plants are consumed as herbal tea across the world and their biol. activity varies depending on the extraction conditions. Furthermore, bioactive compounds are sensitive to environmental conditions when the compounds dissolved in water. The conditions necessary for the effective extraction of bioactive compounds are specific to the target plant and it is a problem for the consumer. Optimization of extraction conditions of lemon balm phenolics could provide useful information for the consumer and food industry. The production of phenolic microcapsules (instant soluble tea) from lemon balm could facilitate herbal tea preparation and reduce the preparation time.

Fish sauce fermentation using *Marinococcus halotolerans* SPQ isolate as a starter culture

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Food Science & Nutrition, Volume 9, Issue 2, 2021

A total of 344 halophilic bacteria were isolated from fish fermentation broths, solar salt crystals, seawater, and muds from ponds of salt pans in Vietnam and subjected to aroma evaluation using fish broth containing 29 ~ 30% (w/v) NaCl. One isolate from a salt crystal with the highest aroma score was selected, identified by using 16S rDNA sequence, and named *Marinococcus halotolerans* SPQ. The GC-MS results of the fish broth fermented by *M. halotolerans* SPQ revealed elevated concentrations of several aroma compounds such as ethyl alcohol, 1-propanol, 1-butyl alcohol, 1-amyl alcohol, and methionol. During the validation tests for *M. halotolerans* SPQ, using 2 kg of anchovy fish in 30% (w/v) NaCl at pH 5.78, the total and amino nitrogen values in the broth increased over time from 15.2 g/L at the beginning to 26.3 g/L at 6th month, with these values being comparable to those of the control. The ammoniacal nitrogen value (2.52 g/L) in the inoculated broth at 6th month was slightly higher than that (2.21 g/L) of control. The histamine content of the fish broth inoculated with *M. halotolerans* SPQ after 6 months was 110.12 mg/L, less than the maximum permitted safety limit of 200 mg/L, indicating it to be safe. Physical parameters, such as the total, amino, ammoniacal nitrogens, and histamine content of fish broth fermented by *M. halotolerans* MPQ met the standards for Vietnamese fish sauces. Two important umami amino acids, aspartic and glutamic acid, were seen to significantly increase, by 23.5% and 35.1%, respectively, even in the extremely harsh fermentation conditions posed by 30% (w/v) NaCl. The color, odor, and taste of the fish sauce fermented by *M. halotolerans* SPQ elicited the highest preference score accorded by the panelists. Taken together, *M. halotolerans* SPQ is a promising starter culture strain for fish sauce fermentation.

Formation of amino acid-derived volatile compounds in dry-cured mackerel (*Scomberomorus niphonius)*: Metabolic pathways involving microorganisms, precursors, and intermediates

Juan Yang, Siliang Wu, Ruijie Mai, Li Lin, Wenhong Zhao, Weidong Bai
Food Chemistry, Volume 364, 2021

This study focuses on the formation mechanism of amino acid-derived volatile compounds (AAVC) in dry-cured mackerel (*Scomberomorus niphonius*) (DCM) during the process. Three kind of AAVC (3-methylbutanal, 3-methylbutanol, and phenylacetaldehyde) were detected in DCM. The content of 3-methylbutanal (14.6 mg/kg) was higher than that of phenylacetaldehyde (12.9 mg/kg), and part of which was reduced to 3-methylbutanol (5.15 mg/kg). While the corresponding intermediate, α-ketoisocaproate (156 μg/kg), was lower than that of phenylpyruvic acid (271 μg/kg), indicating its decarboxylation was limited. Five strains (*Bacillus, Enterobacter, Staphylococcus, Macrococcus,* and *Lactobacillus*) that can produce the relative transaminases and decarboxylases were involved in the production of AAVC. The most dominant strain, *Bacillus* (81.9%), was only involved in the production of 3-methylbutanal. The relative abundance of *Staphylococcus*, the sole phenylpyruvate decarboxylase-producing bacteria, was low, resulting in low product conversion. These results indicated that the production of AAVC is determined by specific microorganisms in the products.

Formation of Pyrazines in Maillard Model Systems: Effects of Structures of Lysine-Containing Dipeptides/Tripeptides

Furong Wang, Hailiang Shen, Ting Liu, Xi Yang, Yali Yang, Yurong Guo
Foods, January 2021, 120(2): 273

At present, most investigations involving the Maillard reaction models have focused on free amino acids (FAAs), whereas the effects of peptides on volatile products are poorly understood. In our study, the formation mechanism of pyrazines, which were detected as characteristic volatiles in sunflower seed oil, from the reaction system of glucose and lysine-containing dipeptides and tripeptides was studied. The effect of the amino acid sequences of the dipeptides and tripeptides on pyrazine formation was further highlighted. Four different dipeptides and six tripeptides were selected. The results showed that the production of pyrazines in the lysine-containing dipeptide models was higher than that in the tripeptide and control models. Compounds 2,5(6)-Dimethylpyrazine and 2,3,5-trimethylpyrazine were the main pyrazine compounds in the dipeptide models. Furthermore, the *C*- or *N*-terminal amino acids of lysine-containing dipeptides can exert an important effect on the formation of pyrazines. In dipeptide models with lysine at the *C*-terminus, the content of total pyrazines followed the order of Arg-Lys > His-Lys; the order of the total pyrazine content was Lys-His > Lys-Arg in dipeptide models with *N*-terminal lysine. Additionally, for the tripeptide models with different amino acid sequences, more pyrazines and a greater variety of pyrazines were detected in the tripeptide models with *N*-terminal lysine/arginine than in the tripeptide models with *N*-terminal histidine. However, the total pyrazine content and the percentage of pyrazines in the total volatiles were similar in the tripeptide models with the same amino acids at the *N*-terminus. This study clearly illustrates the ability of dipeptides and tripeptides containing lysine, arginine and histidine to form pyrazines, improving volatile formation during sunflower seed oil processing.

GC/MSD Pesticide Screening in Strawberries at Tolerance Levels Using Library Searching of Deconvoluted Spectra

Anastasia A. Andrianova, Bruce D. Quimby, Jessica L. Westland
Agilent Technologies, Inc, 2019

The Agilent 8890 GC system and Agilent 5977 GC/MSD system were used for the screening of pesticides in strawberries. With proper selection of instrument configuration, operating conditions, sample preparation, and software workflow, the system provides a robust way to identify pesticides in complex matrices. The hardware was optimized for pesticide detection in foods by incorporating pulsed splitless injection, midcolumn backflush, the Inert Extractor EI source, and retention time locking to a database of pesticides and environmental pollutants. The complete analysis was done in two steps. This application note describes the first step in this workflow whereby samples are screened using Agilent MassHunter Unknowns Analysis software, which provides automated deconvolution and library searching to identify any pesticides or other chemicals of concern. Samples of strawberries were purchased from local grocery stores and were used to demonstrate the capabilities of the method.

Headspace Solid-Phase Microextraction and Ultrasonic Extraction with the Solvent Sequences in Chemical Profiling of *Allium ursinum* L. Honey

Igor Jerković, Piotr M. Kuś
Molecules, Volume 22, Issue 11, Pages 1909, 2017

A volatile profile of ramson (wild garlic, *Allium ursinum* L.) honey was investigated by headspace solid-phase microextraction (HS-SPME) and ultrasonic solvent extraction (USE) followed by gas chromatography and mass spectrometry (GC-FID/GC-MS) analyses. The headspace was dominated by linalool derivatives: *cis*- and *trans*-linalool oxides (25.3%; 9.2%), hotrienol (12.7%), and linalool (5.8%). Besides direct extraction with dichloromethane and pentane/diethyl ether mixture (1:2, *v/v*), two solvent sequences (I: pentane → diethyl ether; II: pentane → pentane/diethyl ether (1:2, *v/v*) → dichloromethane) were applied. Striking differences were noted among the obtained chemical profiles. The extracts with diethyl ether contained hydroquinone (25.8–36.8%) and 4-hydroxybenzoic acid (11.6–16.6%) as the major compounds, while (*E*)-4-(r-1',t-2',c-4'-trihydroxy-2',6',6'-trimethylcyclohexyl)but-3-en-2-one predominated in dichloromethane extracts (18.3–49.1%). Therefore, combination of different solvents was crucial for the comprehensive investigation of volatile organic compounds in this honey type. This particular magastigmane was previously reported only in thymus honey and hydroquinone in vipers bugloss honey, while a combination of the mentioned predominant compounds is unique for *A. ursinum* honey.

Influence of the fatty acid profile on the volatile components of virgin olive oil subjected to thermal stress

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Journal of the Science of Food and Agriculture, August 2021, 101(11): 4829-4837

Background: Virgin olive oil (VOO) is greatly appreciated for its organoleptic features, which can be ascribed mainly to the presence of very chemically diverse volatile components. It is well known that the VOO volatile fraction depends strongly on different aspects, which encompass genetic, agronomic, processing, and post-processing factors. In this research, we developed a method for the qualitative and semiquantitative determination of volatile components in VOOs subjected to thermal stress by headspace extraction online coupled to gas chromatography-mass spectrometry (HS-GC-MS).

Results: The method was applied to 100 extra-virgin olive oil (EVOO) samples, which led to the tentative identification of 52 volatile components, including 12 alcohols, 17 aldehydes, three ketones, one ether, two furans, two carboxylic acids, and 15 hydrocarbons. The method was used to study the cultivar effect and the main biochemical pathways involved in the synthesis of volatile compounds, with special emphasis on those formed by degradation of unsaturated fatty acids (FAs). Principal component analysis (PCA), explaining 76.7% of the total variability, showed that the volatile profile of EVOOs subjected to thermal stress allowed discriminating samples from different cultivars.

Conclusion: Volatiles detected in EVOOs subjected to thermal stress with the highest contribution to discrimination between the selected cultivars were correlated with the concentration of the three main FAs in VOO, namely oleic, linoleic, and linolenic acids. The FA profile seems to be especially relevant to explain the concentration of certain volatile compounds with direct incidence on the organoleptic properties.

Novel fast analytical method for indirect determination of MCPD fatty acid esters in edible oils and fats based on simultaneous extraction and derivatization

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Analytical and Bioanalytical Chemistry, Volume 409, Issue 17, 4267-4278, 2017

A novel method for indirect determination of MCPD esters levels in lipid samples has been developed. The method is based on combination of extraction and derivatization in the same sample preparation step. It is achieved by the application of diethyl ether as extraction solvent for isolation of analytes released from esterified forms from the water phase and as dilution solvent for solid PBA—the derivatization agent. It is a noteworthy improvement of recommended indirect approaches available in the literature because such steps as sample clean-up, multiple liquid–liquid extractions, and preconcentration are excluded in the proposed solution. In this way, the developed procedure is shortened and simplified. Such an approach also minimizes the utilization of organic solvents; therefore, it is in accordance with the principles of "green analytical chemistry." In spite of the fact that the step of sample clean-up is omitted, no deterioration in GC-MS system performance was observed. Equivalence testing of the developed procedure and AOCS cd 29b-13 official method (SGS) has been conducted. It was concluded that results obtained by both methods do not significantly differ statistically. The procedure has been applied to determination of MCPD esters concentrations in lipid fractions isolated by accelerated solvent extraction technique from such foodstuffs as bakery products, salty deep-fried snacks, and instant products. In all investigated samples, the level of bound MCPD was elevated. Additionally, for both procedures, the environmental impact (with the use of analytical Eco-scale) and uncertainty budget have been assessed and compared.

Pesticide Screening in Strawberries Using the Agilent 8860 GC with the Agilent 5977B GC/MSD and SureTarget Deconvolution

Anastasia A. Andrianova, Bruce D. Quimby, Jessica L. Westland
Agilent Technologies, Inc, 2019

The Agilent 8860 GC with the Agilent 5977B GC/MSD system was used for the screening of pesticides in strawberries. This cost-effective system, combined with appropriate sample preparation, operating conditions, and software tools, provides a useful way to identify pesticides and other contaminants in complex matrices such as foods. The instrument configuration incorporated pulsed splitless injection, a stainless steel EI source, and retention time locking to a database of pesticides and environmental pollutants. Complete analysis was done in two steps. Samples were first screened using Agilent MassHunter Unknowns Analysis software, which provides automated deconvolution and library searching to identify any pesticides or other chemicals of concern. Based on the screening results, the sample was then analyzed to quantify any compounds of interest that were found. Samples of strawberries, purchased from local grocery stores, were used to demonstrate the capabilities of the method.

Rapid Rinse and Shoot: Screening Workflow for Pesticides in Fruit by GC/MSD in Under Six Minutes

Anastasia A. Andrianova, Bruce D. Quimby
Agilent Technologies, Inc, 2020

The Agilent Intuvo 9000/5977B GC/MSD system enabled a fast screening workflow for residual pesticides present on the surface of fruits. This method used a GC oven with direct heating technology and MS spectral deconvolution. Residual pesticides were rinsed from the tested commodity surface with acetone. The rinsate was collected and injected into the GC/MSD system. The direct heating oven allowed a very high temperature program rate (250 °C/min) to complete the GC/MS analysis in 3.4 minutes. Spectral deconvolution coupled with the library search algorithm and time-filtering using retention indices resulted in rapid and confident identification of residual pesticides present on the fruit. The NIST 17 spectral library, other commercially available libraries, and user created libraries can be used for compound identification. MassHunter Unknowns Analysis software provides capabilities to create custom reports. The entire analysis from sample collection to reporting took under 6 minutes. The combination of the Intuvo Guard Chip and column backflushing yielded longer maintenance-free uptime. This approach is particularly useful for prioritizing samples for more in-depth analysis.

Species and geographic variability in truffle aromas

Lijdia Strojnik, Tine Grebenc, Nives Ogrinc
Food and Chemical Toxicology, Volume 142, 2020

The gastronomic relevance and price of truffles are related mainly to its unique aroma. In this study, we explore the impact that different volatile compounds have on the aroma quality of fresh truffles using gas chromatography-mass spectrometry (GC-MS). Four hundred sixty fresh ascocarps of nine truffle species (*Tuber aestivum, Tuber magnatum, Tuber melanosporum, Tuber mesentericum, Tuber brumale, Tuber excavatum, Tuber rufum, Tuber indicum* and *Tuber macrosporum*) harvested in 2018/19 and 2019/2020 from 11 different countries (Slovenia, Croatia, Bosnia in Herzegovina, Macedonia, Italy, Spain, France, United Kingdom, Germany, Poland and China) were collected. Our investigation included the classification of species based on their aroma profile, a study of the differences in the volatile organic composition of truffle species over a geographical area, and, in more detail, a study of *T. aestivum* from four natural truffle growing sites in Slovenia. Our models can distinguish between groups, with small classification error. These models could form the basis of a predictive framework to detect fraud concerning truffle products and to determine the influence of different growing parameters on the aroma profile of truffles.

Ecology

10-Methyldodecanal, a Novel Attractant Pheromone Produced by Males of the South American Cerambycid Beetle *Eburodacrys vittata*

Weliton D. Silva, Jocelyn G. Millar, Lawrence M. Hanks, José Maurício S. Bento
PLOS One, Volume 11, Issue 8, 2016

We report the identification, synthesis, and field bioassay of a novel attractant pheromone produced by males of *Eburodacrys vittata* (Blanchard), a South American cerambycid beetle in the subfamily Cerambycinae. Headspace volatiles from males contained a sex-specific compound, identified as 10-methyldodecanal. In a field bioassay conducted in Brazil, significant numbers of males and females were caught in traps baited with synthesized racemic 10-methyldodecanal, consistent with the aggregation-sex pheromones produced by males of many cerambycine species. This compound represents a new structural class of cerambycid pheromones, and it is the first pheromone identified for a species in the tribe Eburiini.

Behavioral Ecology of the Coffee White Stem Borer: Toward Ecology-Based Pest Management of India's Coffee Plantations

Santosh Rajus, Sriraksha Bhagavan, Hinal Kharva, Srinivas Rao, Shannon Olsson
Frontiers in Ecology and Evolution, February 2021

India is the seventh largest producer of coffee with 395,000 tons of coffee exports that earn 10 billion US dollars annually. Two varieties of coffee are grown in India, *Coffea arabica* (arabica) and *Coffea canephora* (robusta). *Xylotrechus quadripes*, commonly known as Coffee White Stem Borer (CWSB), is a major pest of arabica, causing yearly crop damage of 17–40 million dollars. Management strategies, over 100 years in development, have provided successful, yet inconsistent solutions due to differences in local climate, elevation, natural enemies, grower diligence, and other factors. In addition, increased pesticide use affects both pests as well as their natural enemies, which has severe negative impacts on the biodiverse regions where coffee is grown. As a result, our goal is to develop an ecology-based solution for long term management of CWSB that reduces the use of pesticides and focuses on the importance of natural enemies and native hosts. *In situ* behavioral experiments were performed to examine the preferences of CWSB for various local species under field conditions. We found that CWSB beetles were attracted to both healthy arabica and robusta plants, and host plant volatiles played a key role in host selection. In addition, the beetles were attracted to the leaves of these coffee plants and also two species of cut stems from common shade trees; *Spathodea campanulata* (nandi flame) and *Grevillea robusta* (silver oak). Beetles were not attracted toward cut stems of *Tectona grandis* (teak) or *Coffea arabica*. GC-EAD and EAG experiments were then performed to identify host plant volatiles for these species, and these compounds were tested in field conditions to assess their effectiveness against the known chemical attractant pheromone. We found that the CWSB was attracted to our identified host volatile blend as much as the pheromone lure, although trap catches in general were very low. Having an understanding of the behavioral ecology of this pest can form the basis for new methods that use natural attractant and repellent plants to control the pests, reduce the cost of plantation pest management, and avoid the extensive use of insecticides.

The evolution of sexual signaling is linked to odorant receptor tuning in perfume-collecting orchid bees

Philipp Brand, Ismael A. Hinojosa-Díaz, Ricardo Ayala, Michael Daigle, Carmen L. Yurrita Obiols, Thomas Eltz, Santiago R. Ramírez
Nature Communications, 11, 244, 2020

Sexual signaling is an important reproductive barrier known to evolve early during the formation of new species, but the genetic mechanisms that facilitate the divergence of sexual signals remain elusive. Here we isolate a gene linked to the rapid evolution of a signaling trait in a pair of nascent neotropical orchid bee lineages, *Euglossa dilemma* and *E. viridissima*. Male orchid bees acquire chemical compounds from their environment to concoct species-specific perfumes to later expose during courtship. We find that the two lineages acquire chemically distinct perfumes and are reproductively isolated despite low levels of genome-wide differentiation. Remarkably, variation in perfume chemistry coincides with rapid divergence in few odorant receptor (OR) genes. Using functional assays, we demonstrate that the derived variant of *Or41* in *E. dilemma* is specific towards its species-specific major perfume compound, whereas the ancestral variant in *E. viridissima* is broadly tuned to multiple odorants. Our results show that OR evolution likely played a role in the divergence of sexual communication in natural populations.

GC-MS Based Identification of the Volatile Components of Six Astragalus Species from Uzbekistan and Their Biological Activity

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Plants, 2021, 10(1), 124

The compositions of volatile components in the aerial parts of six *Astragalus* species, namely *A. campylotrichus* (*Aca*), *A. chiwensis* (*Ach*), *A. lehmannianus* (*Ale*), *A. macronyx* (*Ama*), *A. mucidus* (*Amu*) and *A. sieversianus* (*Asi*), were investigated using gas chromatograph-mass spectrometry (GC-MS) analysis. Ninety-seven metabolites were identified, accounting for 73.28, 87.03, 74.38, 87.93, 85.83, and 91.39% of *Aca, Ach, Ale, Ama, Amu* and *Asi* whole oils, respectively. Sylvestrene was the most predominant component in A*si, Amu* and *Ama*, with highest concentration in *Asi* (64.64%). In addition, (E)-2-hexenal was present in a high percentage in both *Ale* and *Ach* (9.97 and 10.1%, respectively). GC-MS based metabolites were subjected to principal component analysis (PCA) and hierarchal cluster analysis (HCA) to explore the correlations between the six species. The PCA score plot displayed clear differentiation of all *Astragalus* species and a high correlation between the *Amu* and *Ama* species. The antioxidant activity was evaluated *in vitro* using various assays, phosphomolybdenum (PM), 2,2 diphenyl-1-picryl-hydrazyl-hydrate (DPPH), 2,2-azino bis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), cupric reducing antioxidant capacity (CUPRAC), ferric reducing power (FRAP) and ferrous ion chelation (FIC) assays. In addition, the potential for the volatile samples to inhibit both acetyl/butyrylcholinesterases (AChE, BChE), α- amylase, α-glucosidase and tyrosinase was assessed. Most of the species showed considerable antioxidant potential in the performed assays. In the DPPH assay, *Ama* exhibited the maximum activity (24.12 ± 2.24 mg TE/g sample), and the volatiles from *Amu* exhibited the highest activity (91.54 mgTE/g oil) in the ABTS radical scavenging assay. The effect was more evident in both CUPRAC and FRAP assays, where both *Ale* and *Ama* showed the strongest activity in comparison with the other tested species (84.06, 80.28 mgTE/g oil for CUPRAC and 49.47, 49.02 mgTE/g oil for FRAP, respectively). *Asi* demonstrated the strongest AChE (4.55 mg GALAE/g oil) and BChE (3.61 mg GALAE/g oil) inhibitory effect. Furthermore, the best tyrosinase inhibitory potential was observed for *Ale* (138.42 mg KAE/g). Accordingly, *Astragalus* species can be utilized as promising natural sources for many medicinally important components that could be tested as drug candidates for treating illnesses such as Alzheimer's disease, diabetes mellitus and oxidative stress-related diseases.

Identification of a male-produced sex-aggregation pheromone for a highly invasive cerambycid beetle, *Aromia bungii*

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Scientific Reports, Volume 7, Article number 7330, 2017

The longhorned beetle *Aromia bungii* (Coleoptera: Cerambycidae) is a major pest of stone fruit trees in the genus Prunus, including cherries, apricots, and peaches. Its native range includes China, Korea, Mongolia, and eastern Russia, but it has recently invaded and become established in several countries in Europe, and Japan, and it has been intercepted in shipments coming into North America and Australia. Here, we report the identification of its male-produced aggregation pheromone as the novel compound (E)-2-*cis*-6,7-epoxynonenal. In field trials in its native range in China, and in recently invaded areas of Japan, the pheromone attracted both sexes of the beetle. Thus, the pheromone should find immediate use in worldwide quarantine surveillance efforts to detect the beetle in incoming shipments. The pheromone will also be a crucial tool in ongoing efforts to eradicate the beetle from regions of the world that it has already invaded.

Gut microbiota mediate caffeine detoxification in the primary insect pest of coffee

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Nature Communications, Volume 6, Issue 1, 2015

The coffee berry borer (*Hypothenemus hampei*) is the most devastating insect pest of coffee worldwide with its infestations decreasing crop yield by up to 80%. Caffeine is an alkaloid that can be toxic to insects and is hypothesized to act as a defence mechanism to inhibit herbivory. Here we show that caffeine is degraded in the gut of *H. hampei*, and that experimental inactivation of the gut microbiota eliminates this activity. We demonstrate that gut microbiota in *H. hampei* specimens from seven major coffee-producing countries and laboratory-reared colonies share a core of microorganisms. Globally ubiquitous members of the gut microbiota, including prominent *Pseudomonas* species, subsist on caffeine as a sole source of carbon and nitrogen. *Pseudomonas* caffeine demethylase genes are expressed *in vivo* in the gut of *H. hampei*, and re-inoculation of antibiotic-treated insects with an isolated *Pseudomonas* strain reinstates caffeine-degradation ability confirming their key role.

Male sex pheromone components in *Heliconius* butterflies released by the androconia affect female choice

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PeerJ, Volume 5, e3953, 2017

Sex-specific pheromones are known to play an important role in butterfly courtship, and may influence both individual reproductive success and reproductive isolation between species. Extensive ecological, behavioural and genetic studies of *Heliconius* butterflies have made a substantial contribution to our understanding of speciation. Male pheromones, although long suspected to play an important role, have received relatively little attention in this genus. Here, we combine morphological, chemical and behavioural analyses of male pheromones in the Neotropical butterfly *Heliconius melpomene*. First, we identify putative androconia that are specialized brush-like scales that lie within the shiny grey region of the male hindwing. We then describe putative male sex pheromone compounds, which are largely confined to the androconial region of the hindwing of mature males, but are absent in immature males and females. Finally, behavioural choice experiments reveal that females of *H. melpomene, H. erato* and *H. timareta* strongly discriminate against conspecific males which have their androconial region experimentally blocked. As well as demonstrating the importance of chemical signalling for female mate choice in *Heliconius* butterflies, the results describe structures involved in release of the pheromone and a list of potential male sex pheromone compounds.

Plant volatiles induced by herbivore eggs prime defences and mediate shifts in the reproductive strategy of receiving plants

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Ecology Letters, Volume 3, 7, 1097-1106, 2020

Plants can detect cues associated with the risk of future herbivory and modify defence phenotypes accordingly; however, our current understanding is limited both with respect to the range of early warning cues to which plants respond and the nature of the responses. Here we report that exposure to volatile emissions from plant tissues infested with herbivore eggs promotes stronger defence responses to subsequent herbivory in two *Brassica* species. Furthermore, exposure to these volatile cues elicited an apparent shift from growth to reproduction in *Brassica nigra*, with exposed plants exhibiting increased flower and seed production, but reduced leaf production, relative to unexposed controls. Our results thus document plant defence priming in response to a novel environmental cue, oviposition-induced plant volatiles, while also showing that plant responses to early warning cues can include changes in both defence and life-history traits.

Metabolomics and Proteomics

1,5-Anhydroglucitol predicts CKD progression in macroalbuminuric diabetic kidney disease: results from non-targeted metabolomics

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Metabolomics, February 2018, 14(4): 39

Introduction: Metabolomics allows exploration of novel biomarkers and provides insights on metabolic pathways associated with disease. To date, metabolomics studies on CKD have been largely limited to Caucasian populations and have mostly examined surrogate end points.

Objective: In this study, we evaluated the role of metabolites in predicting a primary outcome defined as dialysis need, doubling of serum creatinine or death in Brazilian macroalbuminuric DKD patients.

Methods: Non-targeted metabolomics was performed on plasma from 56 DKD patients. Technical triplicates were done. Metabolites were identified using Agilent Fiehn GC/MS Metabolomics and NIST libraries (Agilent MassHunter Work-station Quantitative Analysis, version B.06.00). After data cleaning, 186 metabolites were left for analyses.

Results: During a median follow-up time of 2.5 years, the PO occurred in 17 patients (30.3%). In non-parametric testing, 13 metabolites were associated with the PO. In univariate Cox regression, only 1,5-anhydroglucitol (HR 0.10; 95% CI 0.01-0.63, p = .01), norvaline and L-aspartic acid were associated with the PO. After adjustment for baseline renal function, 1,5-anhydroglucitol (HR 0.10; 95% CI 0.02-0.63, p = .01), norvaline (HR 0.01; 95% CI 0.001-0.4, p = .01) and aspartic acid (HR 0.12; 95% CI 0.02-0.64, p = .01) remained significantly and inversely associated with the PO.

Conclusion: Our results show that lower levels of 1,5-anhydroglucitol, norvaline and L-aspartic acid are associated with progression of macroalbuminuric DKD. While norvaline and L-aspartic acid point to interesting metabolic pathways, 1,5-anhydroglucitol is of particular interest since it has been previously shown to be associated with incident CKD. This inverse biomarker of hyperglycemia should be further explored as a new tool in DKD.

Analysis of Mammalian Cell Proliferation and Macromolecule Synthesis Using Deuterated Water and Gas Chromatography-Mass Spectrometry

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Metabolites, 6(4): 34, 2016

Deuterated water (^2H_2O), a stable isotopic tracer, provides a convenient and reliable way to label multiple cellular biomass components (macromolecules), thus permitting the calculation of their synthesis rates. Here, we have combined ^2H_2O labelling, GC-MS analysis and a novel cell fractionation method to extract multiple biomass components (DNA, protein and lipids) from the one biological sample, thus permitting the simultaneous measurement of DNA (cell proliferation), protein and lipid synthesis rates. We have used this approach to characterize the turnover rates and metabolism of a panel of mammalian cells in vitro (muscle C2C12 and colon cancer cell lines). Our data show that in actively-proliferating cells, biomass synthesis rates are strongly linked to the rate of cell division. Furthermore, in both proliferating and non-proliferating cells, it is the lipid pool that undergoes the most rapid turnover when compared to DNA and protein. Finally, our data in human colon cancer cell lines reveal a marked heterogeneity in the reliance on the de novo lipogenic pathway, with the cells being dependent on both 'self-made' and exogenously-derived fatty acid.

Apicoplast-Localized Lysophosphatidic Acid Precursor Assembly Is Required for Bulk Phospholipid Synthesis in *Toxoplasma gondii* and Relies on an Algal/Plant-Like Glycerol 3-Phosphate Acyltransferase

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PLOS Pathogens, Volume 12, Issue 8, 2016

Most apicomplexan parasites possess a non-photosynthetic plastid (the apicoplast), which harbors enzymes for a number of metabolic pathways, including a prokaryotic type II fatty acid synthesis (FASII) pathway. In *Toxoplasma gondii*, the causative agent of toxoplasmosis, the FASII pathway is essential for parasite growth and infectivity. However, little is known about the fate of fatty acids synthesized by FASII. In this study, we have investigated the function of a plant-like glycerol 3-phosphate acyltransferase (*Tg*ATS1) that localizes to the *T. gondii* apicoplast. Knock-down of *TgATS1* resulted in significantly reduced incorporation of FASII-synthesized fatty acids into phosphatidic acid and downstream phospholipids and a severe defect in intracellular parasite replication and survival. Lipidomic analysis demonstrated that lipid precursors are made in, and exported from, the apicoplast for *de novo* biosynthesis of bulk phospholipids. This study reveals that the apicoplast-located FASII and ATS1, which are primarily used to generate plastid galactolipids in plants and algae, instead generate bulk phospholipids for membrane biogenesis in *T. gondii*.

Combined toxic effects of dioxin-like PCB77 with Fe-based nanoparticles in earthworm *Eisenia fetida*

Fan Zhang, Mengyang He, Chunlong Zhang, Daohui Lin, Jianying Zhang
Science of the Total Environment, Volume 766, 2021

Iron-based nanomaterials hold promise for in situ remediation of persistent halogenated contaminants such as dioxin-like polychlorinated biphenyls, however, their complex interactions and joint toxicity toward beneficial soil biological functions remain unknown. This study examined the effects of nano-zero valent iron (nZVI) on the physiological and morphological changes, on the bioaccumulation of co-existed dioxin-like 3,3',4,4'-tetrachloro-biphenyls (PCB77), and the joint toxicity of nZVI and PCB77 in earthworms *Eisenia fetida*. An orthogonally designed experiment was conducted through the exposure of *E. fetida* to the combined and separate nZVI and PCB77 at various concentrations in soil for 28 days (nZVI at the levels of g-Fe/kg-soil and PCB77 at the levels of mg-PCB/kg-soil). Results indicated that both nZVI and PCB77 inhibited the growth and reproduction of earthworms, and the combined exposure resulted in a synergistic effect. The addition of 10 g/kg nZVI decreased the contents of PCB77 and significantly increased the accumulation of PCB77 to a level ranging 14–97 mg/kg in earthworms in a nZVI dose dependent manner. The observed synergism might relate to the aggravated damage of earthworm epidermis in the presence of nZVI. PCB77 and nZVI at their corresponding high levels (10 mg/kg and 10 g/kg) induced oxidative stress and lipid peroxidation in the earthworms through the increased levels of reactive oxygen species and the subsequent inhibition of antioxidant enzymes including superoxide dismutase and catalase. Further metabolomics analyses revealed that the normal glutamic acid metabolism and tricarboxylic acid cycle were disturbed in earthworms exposed to the combined treatment of 10 mg/kg PCB77 and 10 g/kg nZVI. Our findings suggested that earthworms as a sentinel species could be readily employed in toxicity and tolerance studies to succeed the safe applications of nZVI and interestingly earthworms themselves also hold promise for vermiremediation owing to the high bioaccumulation potential of PCBs from contaminated soils.

Distinct urine metabolome after Asian ginseng and American ginseng intervention based on GC-MS metabolomics approach

Liu Yang, Qing-Tao Yu, Ya-Zhong Ge, Wen-Song Zhang, Yong Fan, Chung-Wah Ma, Qun Liu, Lian-Wen Qi
Scientific Reports, 6, 39045, 2016

Ginseng occupies a prominent position in the list of best-selling natural products worldwide. Asian ginseng (*Panax ginseng*) and American ginseng (*Panax quinquefolius*) show different properties and medicinal applications in pharmacology, even though the main active constituents of them are both thought to be ginsenosides. Metabolomics is a promising method to profile entire endogenous metabolites and monitor their fluctuations related to exogenous stimulus. Herein, an untargeted metabolomics approach was applied to study the overall urine metabolic differences between Asian ginseng and American ginseng in mice. Metabolomics analyses were performed using gas chromatography-mass spectrometry (GC-MS) together with multivariate statistical data analysis. A total of 21 metabolites related to D-glutamine and D-glutamate metabolism, glutathione metabolism, TCA cycle and glyoxylate and dicarboxylate metabolism, differed significantly under the Asian ginseng treatment; 34 metabolites mainly associated with glyoxylate and dicarboxylate metabolism, TCA cycle and taurine and hypotaurine metabolism, were significantly altered after American ginseng treatment. Urinary metabolomics reveal that Asian ginseng and American ginseng can benefit organism physiological and biological functions via regulating multiple metabolic pathways. The important pathways identified from Asian ginseng and American ginseng can also help to explore new therapeutic effects or action targets so as to broad application of these two ginsengs.

Exometabolomic Analysis of Cross-Feeding Metabolites

Andrea Lubbe, Benjamin P. Bowen, Trent Northen
Metabolites, Volume 7, Issue 4, 50, 2017

Microbial consortia have the potential to perform complex, industrially important tasks. The design of microbial consortia requires knowledge of the substrate preferences and metabolic outputs of each member, to allow understanding of potential interactions such as competition and beneficial metabolic exchange. Here, we used exometabolite profiling to follow the resource processing by a microbial co-culture of two biotechnologically relevant microbes, the bacterial cellulose degrader *Cellulomonas fimi*, and the oleaginous yeast *Yarrowia lipolytica*. We characterized the substrate preferences of the two strains on compounds typically found in lignocellulose hydrolysates. This allowed prediction that specific sugars resulting from hemicellulose polysaccharide degradation by *C. fimi* may serve as a cross-feeding metabolites to *Y. lipolytica* in co-culture. We also showed that products of ionic liquid-treated switchgrass lignocellulose degradation by *C. fimi* were channeled to *Y. lipolytica* in a co-culture. Additionally, we observed metabolites, such as shikimic acid accumulating in the co-culture supernatants, suggesting the potential for producing interesting co-products. Insights gained from characterizing the exometabolite profiles of individual and co-cultures of the two strains can help to refine this interaction, and guide strategies for making this an industrially viable co-culture to produce valuable products from lignocellulose material.

Extracellular volatilomic alterations induced by hypoxia in breast cancer cells

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Metabolomics, January 2020, 16(2): 21

Introduction: The metabolic shift induced by hypoxia in cancer cells has not been explored at volatilomic level so far. The volatile organic metabolites (VOMs) constitute an important part of the metabolome and their investigation could provide us crucial aspects of hypoxia driven metabolic reconfiguration in cancer cells.

Objective: To identify the altered volatilomic response induced by hypoxia in metastatic/aggressive breast cancer (BC) cells.

Methods: BC cells were cultured under normoxic and hypoxic conditions and VOMs were extracted using HS-SPME approach and profiled by standard GC-MS system. Univariate and multivariate statistical approaches ($p < 0.05$, Log_2 FC ≥ 0.58/≤ - 0.58, PC1 > 0.13/< - 0.13) were applied to select the VOMs differentially altered after hypoxic treatment. Metabolic pathway analysis was also carried out in order to identify altered metabolic pathways induced by the hypoxia in the selected BC cells.

Results: Overall, 20 VOMs were found to be significantly altered ($p < 0.05$, PC1 > 0.13/< - 0.13) upon hypoxic exposure to BC cells. Further, cell line specific volatilomic alterations were extracted by comparative metabolic analysis of aggressive (MDA-MB-231) vs. non-aggressive (MCF-7) cells incubated under hypoxia and normoxia. In this case, 15 and 12 VOMs each were found to be significantly altered in aggressive cells when exposed to hypoxic and normoxic condition respectively. Out of these, 9 VOMs were found to be uniquely associated with hypoxia, 6 were specific to normoxia and 6 were found common to both the conditions. Formic acid was identified as the most prominent molecule with higher abundance levels in aggressive as compared to non-aggressive cells in both conditions. Furthermore, metabolic pathway analyses revealed that fatty acid biosynthesis and nicotinate and nicotinamide metabolism were significantly altered in aggressive as compared to non-aggressive cells in normoxia and hypoxia respectively.

Conclusions: Higher formate overflow was observed in aggressive cells compared to non-aggressive cells incubated under both the conditions, reinforcing its correlation with aggressive and invasive cancer type. Moreover, under hypoxia, aggressive cells preferred to be bioenergetically more efficient whereas, under normoxia, fatty acid biosynthesis was favoured when compared to non-aggressive cells.

GC–MS metabolic profiling reveals fructose-2,6-bisphosphate regulates branched chain amino acid metabolism in the heart during fasting

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Metabolomics, 15, 18, 2019

Introduction: As an insulin sensitive tissue, the heart decreases glucose usage during fasting. This response is mediated, in part, by decreasing phosphofructokinase-2 (PFK-2) activity and levels of its product fructose-2,6-bisphosphate. However, the importance of fructose-2,6-bisphosphate in the fasting response on other metabolic pathways has not been evaluated.

Objectives: The goal of this study is to determine how sustaining cardiac fructose-2,6-bisphosphate levels during fasting affects the metabolomic profile.

Methods: Control and transgenic mice expressing a constitutively active form of PFK-2 ($Glyco^{Hi}$) were subjected to either 12-h fasting or regular feeding. Animals (n = 4 per group) were used for whole-heart extraction, followed by gas chromatography–mass spectrometry metabolic profiling and multivariate data analysis.

Results: Principal component analysis displayed differences between Control and $Glyco^{Hi}$ groups under both fasting and fed conditions while a clear response to fasting was observed only for Control animals. However, pathway analysis revealed that these smaller changes in the $Glyco^{Hi}$ group were significantly associated with branched-chain amino acid (BCAA) metabolism (~ 40% increase in all BCAAs). Correlation network analysis demonstrated clear differences in response to fasting between Control and $Glyco^{Hi}$ groups amongst most parameters. Notably, fasting caused an increase in network density in the Control group from 0.12 to 0.14 while the $Glyco^{Hi}$ group responded oppositely (0.17–0.15).

Conclusions: Elevated cardiac PFK-2 activity during fasting selectively increases BCAAs levels and decreases global changes in metabolism.

A fungal transcription factor essential for starch degradation affects integration of carbon and nitrogen metabolism

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PLOS Genetics, Volume 13, Issue 5, 2017

In *Neurospora crassa*, the transcription factor COL-26 functions as a regulator of glucose signaling and metabolism. Its loss leads to resistance to carbon catabolite repression. Here, we report that COL-26 is necessary for the expression of amylolytic genes in *N. crassa* and is required for the utilization of maltose and starch. Additionally, the Δ*col-26* mutant shows growth defects on preferred carbon sources, such as glucose, an effect that was alleviated if glutamine replaced ammonium as the primary nitrogen source. This rescue did not occur when maltose was used as a sole carbon source. Transcriptome and metabolic analyses of the Δ*col-26* mutant relative to its wild type parental strain revealed that amino acid and nitrogen metabolism, the TCA cycle and GABA shunt were adversely affected. Phylogenetic analysis showed a single *col-26* homolog in Sordariales, Ophilostomatales, and the Magnaporthales, but an expanded number of *col-26* homologs in other filamentous fungal species. Deletion of the closest homolog of *col-26* in *Trichoderma reesei, bglR*, resulted in a mutant with similar preferred carbon source growth deficiency, and which was alleviated if glutamine was the sole nitrogen source, suggesting conservation of COL-26 and BglR function. Our finding provides novel insight into the role of COL-26 for utilization of starch and in integrating carbon and nitrogen metabolism for balanced metabolic activities for optimal carbon and nitrogen distribution.

Gut metabolomics profiling of non-small cell lung cancer (NSCLC) patients under immunotherapy treatment

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Journal of Translational Medicine, 18, 49, 2020

Background: Despite the efficacy of immune checkpoint inhibitors (ICIs) only the 20–30% of treated patients present long term benefits. The metabolic changes occurring in the gut microbiota metabolome are herein proposed as a factor potentially influencing the response to immunotherapy.

Methods: The metabolomic profiling of gut microbiota was characterized in 11 patients affected by non-small cell lung cancer (NSCLC) treated with nivolumab in second-line treatment with anti-PD-1 nivolumab. The metabolomics analyses were performed by GC–MS/SPME and ^{1}H-NMR in order to detect volatile and non-volatile metabolites. Metabolomic data were processed by statistical profiling and chemometric analyses.

Results: Four out of 11 patients (36%) presented early progression, while the remaining 7 out of 11 (64%) presented disease progression after 12 months. 2-Pentanone (ketone) and tridecane (alkane) were significantly associated with early progression, and on the contrary short chain fatty acids (SCFAs) (i.e., propionate, butyrate), lysine and nicotinic acid were significantly associated with long-term beneficial effects.

Conclusions: Our preliminary data suggest a significant role of gut microbiota metabolic pathways in affecting response to immunotherapy. The metabolic approach could be a promising strategy to contribute to the personalized management of cancer patients by the identification of microbiota-linked “indicators” of early progressor and long responder patients.

Loss of succinate dehydrogenase activity results in dependency on pyruvate carboxylation for cellular anabolism

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Nature Communications, Volume 6, Issue 1, 2015

The tricarboxylic acid (TCA) cycle is a central metabolic pathway responsible for supplying reducing potential for oxidative phosphorylation and anabolic substrates for cell growth, repair and proliferation. As such it is thought to be essential for cell proliferation and tissue homeostasis. However, since the initial report of an inactivating mutation in the TCA cycle enzyme complex, succinate dehydrogenase (SDH) in paraganglioma (PGL), it has become clear that some cells and tissues are not only able to survive with a truncated TCA cycle, but that they are also able of supporting proliferative phenotype observed in tumours. Here, we show that loss of SDH activity leads to changes in the metabolism of non-essential amino acids. In particular, we demonstrate that pyruvate carboxylase is essential to re-supply the depleted pool of aspartate in SDH-deficient cells. Our results demonstrate that the loss of SDH reduces the metabolic plasticity of cells, suggesting vulnerabilities that can be targeted therapeutically.

Untargeted metabolomics analysis of the upper respiratory tract of ferrets following influenza A virus infection and oseltamivir treatment

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Metabolomics, 15, 33, 2019

Introduction: Influenza is a highly contagious respiratory disease that causes high global morbidity and mortality each year. The dynamics of an influenza infection on the host metabolism, and how metabolism is altered in response to neuraminidase inhibitor drug therapy, is still in its infancy but of great importance.

Objectives: We aim to investigate the suitability of ferret nasal wash samples for metabolomics-based analysis and characterization of influenza infections and oseltamivir treatment.

Methods: Virological and metabolic analyses were performed on nasal wash samples collected from ferrets treated with oseltamivir or a placebo. Untargeted metabolomics was performed using a gas chromatography coupled with mass spectrometery (GC-MS) based protocol that comprised a retention time (RT) locked method and the use of a commercial metabolomics library.

Results: Ferret activity was reduced at 2–3 days post infection, which coincided with the highest influenza viral titre. The metabolomics data indicated a shift in metabolism during various stages of infection. The neuraminidase inhibitor oseltamivir created considerable downregulation of energy center metabolites (glucose, sucrose, glycine and glutamine), which generated high levels of branched amino acids. This further increased branched amino acid degradation and deregulation via glycerate-type intermediates and biosynthesis of fatty acids in oseltamivir-treated animals where abrogated weight loss was observed.

Conclusion: Metabolomics was used to profile influenza infection and antiviral drug treatment in ferrets. This has the potential to provide indicators for the early diagnosis of influenza infection and assess the effectiveness of drug therapies.

Altered Gut Microbial Metabolites in Amnestic Mild Cognitive Impairment and Alzheimer's Disease: Signals in Host-Microbe Interplay

Li Wu, Yuqiu Han, Zhipeng Zheng, Guoping Peng, Ping Liu, Siqing Yue, Shuai Zhu, Jun Chen, Hanying Lv, Lifang Shao, Yan Sheng, Yulan Wang, Liang Li, Lanjuan Li, Baohong Wang
Nutrients, January 2021, 13(1): 228

Intimate metabolic host-microbiome crosstalk regulates immune, metabolic, and neuronal response in health and disease, yet remains untapped for biomarkers or intervention for disease. Our recent study identified an altered microbiome in patients with pre-onset amnestic mild cognitive impairment (aMCI) and dementia Alzheimer's disease (AD). Thus, we aimed to characterize the gut microbial metabolites among AD, aMCI, and healthy controls (HC). Here, a cohort of 77 individuals (22 aMCI, 27 AD, and 28 HC) was recruited. With the use of liquid-chromatography/gas chromatography mass spectrometry metabolomics profiling, we identified significant differences between AD and HC for tryptophan metabolites, short-chain fatty acids (SCFAs), and lithocholic acid, the majority of which correlated with altered microbiota and cognitive impairment. Notably, tryptophan disorders presented in aMCI and SCFAs decreased progressively from aMCI to AD. Importantly, indole-3-pyruvic acid, a metabolite from tryptophan, was identified as a signature for discrimination and prediction of AD, and five SCFAs for pre-onset and progression of AD. This study showed fecal-based gut microbial signatures were associated with the presence and progression of AD, providing a potential target for microbiota or dietary intervention in AD prevention and support for the host-microbe crosstalk signals in AD pathophysiology.

A Biological Route to Conjugated Alkenes: Microbial Production of Hepta-1,3,5-triene

Hanan L. Messiha, Karl A. P. Payne, Nigel S. Scrutton, David Leys
ACS Synthetic Biology, 2021, 10, 2, 228-235

Conjugated alkenes such as dienes and polyenes have a range of applications as pharmaceutical agents and valuable building blocks in the polymer industry. Development of a renewable route to these compounds provides an alternative to fossil fuel derived production. The enzyme family of the UbiD decarboxylases offers substantial scope for alkene production, readily converting poly unsaturated acids. However, biochemical pathways producing the required substrates are poorly characterized, and UbiD-application has hitherto been limited to biological styrene production. Herein, we present a proof-of-principle study for microbial production of polyenes using a bioinspired strategy employing a polyketide synthase (PKS) in combination with a UbiD-enzyme. Deconstructing a bacterial iterative type II PKS enabled repurposing the broad-spectrum antibiotic andrimid biosynthesis pathway to access the metabolic intermediate 2,4,6-octatrienoic acid, a valuable chemical for material and pharmaceutical industry. Combination with the fungal ferulic acid decarboxylase (Fdc1) led to a biocatalytic cascade-type reaction for the production of hepta-1,3,5-triene in vivo. Our approach provides a novel route to generate unsaturated hydrocarbons and related chemicals and provides a blue-print for future development and application.

Biosynthesis of (R)-(-)-1-Octen-3-ol in Recombinant *Saccharomyces cerevisiae* with Lipoxygenase-1 and Hydroperoxide Lyase Genes from *Tricholoma matsutake*

Nan-Yeong Lee, Doo-Ho Choi, Mi-Gyeong Kim, Min-Ji Jeong, Hae-Jun Kwon, Dong-Hyun Kim, Young-Guk Kim, Eric di Luccio, Manabu Arioka, Hyeok-Jun Yoon, Jong-Guk Kim
Journal of Microbiology and Biotechnology, February 2020, 30(2): 296-305

Tricholoma matsutake is an ectomycorrhizal fungus, related with the host of *Pinus densiflora*. Most of studies on *T. matsutake* have focused on mycelial growth, genes and genomics, phylogenetics, symbiosis, and immune activity of this strain. *T. matsutake* is known for its unique fragrance in Eastern Asia. The most major component of its scent is (R)-(-)-1-octen-3-ol and is biosynthesized from the substrate linoleic acid by the sequential reaction of lipoxygenase and peroxide lyase. Here, we report for the first time the biosynthesis of (R)-(-)- 1-octen-3-ol of *T. matsutake* using the yeast *Saccharomyces cerevisiae* as a host. In this study, cDNA genes correlated with these reactions were cloned from T. *matsutake*, and expression studies of theses genes were carried out in the yeast *Saccharomyces cerevisiae*. The product of these genes expression study was carried out with Western blotting. The biosynthesis of (R)-(-)- 1-octen-3-ol of *T. matsutake* in recombinant *Saccharomyces cerevisiae* was subsequently identified with GC-MS chromatography analysis. The biosynthesis of (R)-(-)-1-octen-3-ol with *S. cerevisiae* represents a significant step forward.

Determination of residual monomer content in dental acrylic polymers and effect after tissues implantation

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Biotechnology & Biotechnological Equipment, 34:1, 254-263, 2020

The aim of the present study was to determine the content of residual monomer methyl methacrylate (MMA) in cold and hot polymerized poly(methyl methacrylate) (PMMA), both widely applicable in dentistry, by using MHE-GC-MS (multiple headspace extraction analysis by gas chromatography-mass spectrometry) in combination with GC-FID (gas chromatography with flame-ionization detection). The samples of PMMA were obtained by free-radical polymerization of MMA at room temperature (cold polymerized PMMA) and at 100 °C (hot polymerized PMMA), according to the manufacturer's instructions. The MHE-GC-MS method consisted of ten successive extractions of MMA from the polymerized samples. According to the constructed calibration curve, the content of residual MMA in PMMA samples (mg_{MMA}/g_{PMMA}) was determined. Intramuscular implantation of sample materials was performed in experimental animals (rats) in order to demonstrate potential adverse effects of the unpolymerized residual reactants to the tissue in direct contact with polymeric implants. The content of residual monomer in cold polymerized PMMA was higher (15.75 mg_{MMA}/g_{PMMA}) in comparison to hot polymerized PMMA (10.96 mg_{MMA}/g_{PMMA}). The implanted samples of cold-polymerized acrylic resin showed intense inflammatory response of the surrounding tissue. According to the obtained results, hot polymerized PMMA is safer for use in dentistry.

Development of a new methodology for the determination of N-nitrosamines impurities in ranitidine pharmaceuticals using microextraction and gas chromatography-mass spectrometry

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Talanta, Volume 223, Part 2, 2021

Ranitidine drug products were recently recalled because they contained carcinogenic nitrosamines (NAs), such as N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA). This episode emphasises the importance of developing analytical methods to determine NAs in this type of product. This study describes the development and validation of an analytical method for the determination of nine NAs (NDMA, N-nitrosomethylethylamine (NEMA), NDEA, N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR) N-nitrosodi-n-propylamine (NDPA) N-nitrosopiperidine (NPIP), N-nitrosodi-n-butylamine (NDBA) and N-nitrosodiphenylamine (NDPhA)) in ranitidine drug samples using a combination of microextraction and gas chromatography-mass spectrometry. The procedure involved the dissolution of 1 g of sample in 10 mL of water. For the dispersive liquid-liquid microextraction, 0.5 g of NaCl was added to this aqueous solution, followed by a mixture containing 0.5 mL methanol as dispersant and 150 µL chloroform as extractant solvent. The recovered organic phase was injected into the GC-MS system and a 20 min oven programme was applied. Quantification limits were in the 0.21–21 ng g^{-1} range, corresponding the lower limit to NDPhA and the higher to NDMA. Relative standard deviations lower than 12% were achieved in all cases, which indicates the adequate precision of the method. Seven pharmaceutical products containing two different amounts of ranitidine (150 and 300 mg) were analysed. None of the samples contained NEMA, NDEA, NPYR, NMOR, NDPA or NPIP, while NDMA, NDBA and NDPhA were found in three products.

Development of a novel hyaluronic acid membrane for the treatment of ocular surface diseases

Dong Ju Kim, Mi-Young Jung, Ha-Jin Pak, Joo-Hee Park, Martha Kim, Roy S. Chuck, Choul Yong Park
Scientific Reports, 11(1): 2351, 2021

Ocular surface diseases (OSD) can cause serious visual deterioration and discomfort. Commercial artificial tear solution containing hyaluronic acid (HA) show excellent biocompatibility and unique viscoelastic characteristics. Here, we developed a novel HA membrane (HAM) by chemical crosslinking using 1,4-butanediol diglycidyl ether for the effective treatment of OSDs. The main purpose of HAMs is to provide sustained release of HA to modulate the wound healing response in OSDs. The safety and efficacy of HAMs were investigated using primary cultured human corneal epithelial cells and various OSD rabbit models. In the dry state, the HAM is firm, transparent, and easy to manipulate. When hydrated, it swells rapidly with high water retention and over 90% transmission of visible light. Human corneal epithelial cells and rabbit eyes showed no toxic response to HAM. Addition of HAMs to the culture medium enhanced human corneal epithelial cell viability and expression of cell proliferation markers. Investigation of HAM wound healing efficacy using mechanical or chemical corneal trauma and conjunctival surgery in rabbits revealed that application of HAMs to the ocular surface enhanced healing of corneal epithelium and reduced corneal limbal vascularization, opacity and conjunctival fibrosis. The therapeutic potential of HAMs in various OSDs was successfully demonstrated.

Di-*tert*-butyl Phosphonate Route to the Antiviral Drug Tenofovir

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Organic Process Research and Development, 2021, 25, 4, 789-798

Di-*tert*-butyl oxymethyl phosphonates were investigated regarding their suitability for preparing the active pharmaceutical ingredient tenofovir (PMPA). First, an efficient and simple access to the crystalline di-*tert*-butyl(hydroxymethyl)phosphonate was developed. O-Mesylation gave high yields of the active phosphonomethylation reagent. For the synthesis of tenofovir, a two-step sequence was developed using $Mg(O^tBu)_2$ as the base for the alkylation of (R)-9-(2-hydroxypropyl)adenine. Subsequent deprotection could be achieved with aqueous acids. (Di-*tert*-butoxyphosphoryl)methyl methanesulfonate showed to be the most efficient electrophile tested, affording PMPA in 72% yield on a 5 g scale. The developed protocol could also be applied for the preparation of the hepatitis B drug adefovir (64% yield/1 g scale).

Involvement of organic acids and amino acids in ameliorating Ni(II) toxicity induced cell cycle dysregulation in *Caulobacter crescentus*: a metabolomics analysis

Abhishek Jain, Wei-Ning Chen,
Applied Microbiology and Biotechnology, 102, 4563-4575, 2018

Nickel (Ni(II)) toxicity is addressed by many different bacteria, but bacterial responses to nickel stress are still unclear. Therefore, we studied the effect of Ni(II) toxicity on cell proliferation of α-proteobacterium *Caulobacter crescentus*. Next, we showed the mechanism that allows C. crescentus to survive in Ni(II) stress condition. Our results revealed that the growth of *C. crescentus* is severely affected when the bacterium was exposed to different Ni(II) concentrations, 0.003 mM slightly affected the growth, 0.008 mM reduced the growth by 50%, and growth was completely inhibited at 0.015 mM. It was further shown that Ni(II) toxicity induced mislocalization of major regulatory proteins such as MipZ, FtsZ, ParB, and MreB, resulting in dysregulation of the cell cycle. GC-MS metabolomics analysis of Ni(II) stressed *C. crescentus* showed an increased level of nine important metabolites including TCA cycle intermediates and amino acids. This indicates that changes in central carbon metabolism and nitrogen metabolism are linked with the disruption of cell division process. Addition of malic acid, citric acid, alanine, proline, and glutamine to 0.015 mM Ni(II)-treated *C. crescentus* restored its growth. Thus, the present work shows a protective effect of these organic acids and amino acids on Ni(II) toxicity. Metabolic stimulation through the PutA/GlnA pathway, accelerated degradation of CtrA, and Ni-chelation by organic acids or amino acids are some of the possible mechanisms suggested to be involved in enhancing *C. crescentus*'s tolerance. Our results shed light on the mechanism of increased Ni(II) tolerance in *C. crescentus* which may be useful in bioremediation strategies and synthetic biology applications such as the development of whole cell biosensor.

An oleaginous yeast platform for renewable 1-butanol synthesis based on a heterologous CoA-dependent pathway and an endogenous pathway

Aiqun Yu, Yakun Zhao, Yaru Pang, Zhihui Hu, Cuiying Zhang, Dongguang Xiao, Matthew Wook Chang, Susanna Su Jan Leong
Microbial Cell Factories, 17, 166, 2018

Background: Microbial biofuel production provides a promising sustainable alternative to fossil fuels. 1-Butanol is recognized as an advanced biofuel and is gaining attention as an ideal green replacement for gasoline. In this proof-of-principle study, the oleaginous yeast *Yarrowia lipolytica* was first engineered with a heterologous CoA-dependent pathway and an endogenous pathway, respectively.

Results: The co-overexpression of two heterologous genes *ETR1* and *EutE* resulted in the production of 1-butanol at a concentration of 65 µg/L. Through the overexpression of multiple 1-butanol pathway genes, the titer was increased to 92 µg/L. Cofactor engineering through endogenous overexpression of a glyceraldehyde-3-phosphate dehydrogenase and a malate dehydrogenase further led to titer improvements to 121 µg/L and 110 µg/L, respectively. In addition, the presence of an endogenous 1-butanol production pathway and a gene involved in the regulation of 1-butanol production was successfully identified in *Y. lipolytica*. The highest titer of 123.0 mg/L was obtained through this endogenous route by combining a pathway gene overexpression strategy.

Conclusions: This study represents the first report on 1-butanol biosynthesis in *Y. lipolytica*. The results obtained in this work lay the foundation for future engineering of the pathways to optimize 1-butanol production in *Y. lipolytica*.

Photocatalytic degradation of selected pharmaceuticals using g-C3N4 and TiO2 nanomaterials

Aneta Smykalova, Barbora Skolova, Krystof Foniok, Vlastimil Matejka, Petr Praus
Nanomaterials, 2019, 9(9); 1194

Exfoliated graphitic carbon nitride (g-C_3N_4) and two commercially available nanomaterials from titanium dioxide (P25 and CG300) were tested for the photocatalytic degradation of paracetamol (PAR), ibuprofen (IBU), and diclofenac (DIC). Prior to photocatalytic experiments, the nanomaterials were characterized by common methods, such as X-ray diffraction (XRD), UV–VIS diffuse reflectance spectroscopy (DRS), Fourier transformed infrared spectroscopy in attenuated total reflection mode (FTIR–ATR), transmission electron microscopy (TEM), physisorption of nitrogen, and dynamic vapor adsorption (DVS) of water. The sizes and specific surface area (SSA) of the TiO_2 nanoparticles were 6 nm and 300 $m^2 \cdot g^{-1}$ for CG300 and 21 nm and 50 $m^2 \cdot g^{-1}$ for P25. The SSA of g-C_3N_4 was 140 $m^2 \cdot g^{-1}$. All photocatalytic experiments were performed under UV (368 nm), as well as VIS (446 nm) irradiation. TiO_2 P25 was the most active photocatalyst under UV irradiation and g-C_3N_4 was the most active one under VIS irradiation. Photodegradation yields were evaluated by means of high performance liquid chromatography (HPLC) and reaction intermediates were identified using gas chromatography with mass detection (GC–MS). Paracetamol and ibuprofen were totally removed but the intermediates of diclofenac were observed even after 6 h of irradiation. Some intermediates, such as carbazole-1-acetic acid, 2,6-dichloraniline, and hydroxylated derivates of diclofenac were identified. This study showed that g-C_3N_4 is a promising photocatalyst for the degradation of pharmaceuticals in an aqueous environment, under visible light.

Replication Study: The common feature of leukemia-associated IDH1 and IDH2 mutations is a neomorphic enzyme activity converting alpha-ketoglutarate to 2-hydroxyglutarate

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eLife, 6: e2603, 2017

In 2016, as part of the Reproducibility Project: Cancer Biology, we published a Registered Report (Fiehn et al., 2016), that described how we intended to replicate selected experiments from the paper "The common feature of leukemia-associated IDH1 and IDH2 mutations is a neomorphic enzyme activity converting alpha-ketoglutarate to 2-hydroxyglutarate" (Ward *et al.*, 2010). Here, we report the results of those experiments. We found that cells expressing R172K mutant IDH2 did not display isocitrate-dependent NADPH production above vector control levels, in contrast to the increased production observed with wild-type IDH2. Conversely, expression of R172K mutant IDH2 resulted in increased alpha-ketoglutarate-dependent consumption of NADPH compared to wild-type IDH2 or vector control. These results are similar to those reported in the original study (Figure 2; Ward et al., 2010). Further, expression of R172K mutant IDH2 resulted in increased 2HG levels within cells compared to the background levels observed in wild-type IDH2 and vector control, similar to the original study (Figure 3D; Ward et al., 2010). In primary human AML samples, the 2HG levels observed in samples with mutant *IDH1* or *IDH2* status were higher than those observed in samples without an *IDH* mutation, similar to what was observed in the original study (Figure 5C; Ward et al., 2010). Finally, we report meta-analyses for each result.

Whole-cell biocatalytic and de novo production of alkanes from free fatty acids in *Saccharomyces cerevisiae*

Jee Loon Foo, Adelia Vicanatalita Susanto, Jay D. Keasling, Susanna Su Jan Leong, Matthew Wook Chang
Biotechnology and Bioengineering, Volume 114, Issue 1, 232–237, 2017

Rapid global industrialization in the past decades has led to extensive utilization of fossil fuels, which resulted in pressing environmental problems due to excessive carbon emission. This prompted increasing interest in developing advanced biofuels with higher energy density to substitute fossil fuels and bio-alkane has gained attention as an ideal drop-in fuel candidate. Production of alkanes in bacteria has been widely studied but studies on the utilization of the robust yeast host, *Saccharomyces cerevisiae*, for alkane biosynthesis have been lacking. In this proof-of-principle study, we present the unprecedented engineering of *S. cerevisiae* for conversion of free fatty acids to alkanes. A fatty acid α-dioxygenase from *Oryza sativa* (rice) was expressed in *S. cerevisiae* to transform C_{12-18} free fatty acids to C_{11-17} aldehydes. Co-expression of a cyanobacterial aldehyde deformylating oxygenase converted the aldehydes to the desired alkanes. We demonstrated the versatility of the pathway by performing whole-cell biocatalytic conversion of exogenous free fatty acid feedstocks into alkanes as well as introducing the pathway into a free fatty acid overproducer for de novo production of alkanes from simple sugar. The results from this work are anticipated to advance the development of yeast hosts for alkane production.

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