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Review

Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: A review

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HIGHLIGHTS

- Current analytical techniques for POPs in environment and biota are reviewed.
- The review covers most updated literatures reports on POPs analysis.
- For the first time, analysis of new POPs under Stockholm Convention is reviewed.
- Future perspectives on POPs, especially the potential POPs, are discussed.

GRAPHICAL ABSTRACT

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ABSTRACT

Persistent organic pollutants (POPs) are major environmental concern due to their persistence, long-range transportability, bio-accumulation and potentially adverse effects on living organisms. Analytical chemistry plays an essential role in the measurement of POPs and provides important information on their distribution and environmental transformations. Much effort has been devoted during the last two decades to the development of faster, safer, more reliable and more sensitive analytical techniques for these pollutants. Since the Stockholm Convention (SC) on POPs was adopted 12 years ago, analytical methods have been extensively developed. This review article introduces recent analytical techniques and applications for the determination of POPs in environmental and biota samples, and summarizes the extraction, separation and instrumental analyses of the halogenated POPs. Also, this review covers important aspects for the analyses of SC POPs (e.g. lipid determination and quality assurance/quality control (QA/QC)), and finally discusses future trends for improving the POPs analyses and for potential new POPs.

Abbreviations: AMAP, Arctic monitoring and assessment programme; APCI, Atmospheric pressure chemical ionization; BDE, Brominated diphenyl ether; BFR, Brominated flame retardant; CPE, Cloud point extraction; CRM, Certified reference material; DCM, Dichloromethane; DDD, Dichlorodiphenyldichloroethane; DDE, Dichlorodiphenyldichloroethylene; DDT, Dichlorodiphenyltrichloroethane; DL-PCBs, Dioxin-like PCBs; ECD, Electron capture detector; ECNI-MS, Electron capture negative ion mass spectrometry; EI, Electron ionization; ESI, Electrospray ionization; EU/CEN, European Union/Comité Européen de Normalisation; GC, Gas chromatography; GC × GC, Comprehensive two-dimensional gas chromatography; GMP, Global monitoring plan; HBCD, Hexabromocyclododecane; HCB, Hexachlorobenzene; HCH, Hexachlorocyclohexane; HRMS, High resolution mass spectrometry; ITMS, Ion trap mass spectrometry; JIS, Japanese industrial standards; LC, Liquid chromatography; LRAT, Long-range atmospheric transport; LLE, Liquid–liquid extraction; LOD, Limit of detection; MAE, Microwave assisted extraction; MS, Mass spectrometry; NIST, National Institute of Standards and Technology; OCP, Organic chlorinated pesticide; PBDE, Polybrominated diphenyl ether; PCB, Polychlorinated biphenyl; PCDD, Polychlorinated dibenzo-*p*-dioxin; PCDE, Polychlorinated diphenyl ether; PCDF, Polychlorinated dibenzofuran; PCN, Polychlorinated naphthalene; PFAS, Per- and polyfluoroalkylated substances; PFCA, Perfluoroalkyl carboxylic acid; PFOA, Perfluorooctanic acid; PFOS, Perfluorooctane sulfonic acid; PFOSF, Perfluorooctane sulfonyl fluoride; PFSA, Perfluoroalkyl sulfonic acid; PLE, Pressurized liquid extraction; POPs, Persistent organic pollutants; POPRC, Persistent organic pollutants review committee; PUF, Polyurethane foam; QA/QC, Quality assurance and quality control; SC, Stockholm Convention; SCCP, Short-chain chlorinated paraffins; SFE, Supercritical fluid extraction; SIM, Selected ion monitoring; SPE, Solid-phase extraction; SPMD, Semi-permeable membrane device; SPME, Solid-phase microextraction; TBBPA, Tetrabromobisphenol A; UAE, Ultrasonic assisted extraction; UNEP, United Nation Environment Programme; UPLC, Ultra-performance liquid chromatography; USEPA, U.S. Environmental Protection Agency; WHO, World Health Organization.

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Contents

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Prof. Zongwei Cai graduated from Xiamen University, China with Bachelor degree in Chemistry in 1982 and University of Marburg, Germany with Ph.D. degree in Analytical Chemistry in 1990. Currently he is Chair Professor of Chemistry and Director of Dioxin Laboratory, Hong Kong Baptist University. The major research interest of Prof. Cai is method development and applications of chromatography coupled with mass spectrometry for trace environmental analysis. Prof. Cai has been invited to join Asian-Pacific Regional Organization Group for Stockholm Convention on POPs. He is the principal author in Asian-Pacific regional report on POPs under the Stockholm Convention.

1. Introduction

Persistent organic pollutants (POPs) are a group of chemicals that have been intentionally or inadvertently produced and introduced into the environment. Due to their stability and long-range transport properties, they are now ubiquitous around the world and are even found in places such as the arctic regions, far distant from where they had been intensively used. Because of their high fat solubility, such chemicals tend to bio-accumulate in animals, especially in species at the top of the food chain. POPs appear at higher concentrations in fat-containing foods, including fish, meat, eggs and milks, and so traces of POPs are found in the human body. Some cancers, birth defects, dysfunctional immune and reproductive systems and even diminished intelligence are suspected to be related to an exposure to these chemicals. The Stockholm Convention (SC) on POPs was adopted on May, 2001 and came into force in 2004 [1]. It is a global treaty under the United Nation Environment Programme (UNEP), with the participation of 171 countries and one regional economic integration organization. The SC aim is to protect humans and the environment from hazardous and persistent chemicals by reducing or eliminating their production and introduction to the environment. The initial SC list in 2004 included 12 chemicals called the “dirty dozen”. In August 2009, nine new chemicals were added in an amendment and came into force 1 year later. During the fifth meeting held in 2011, endosulfan became the 22nd POP.

The development of analytical methods for POPs provides reliable data for their environmental and biological occurrence and therefore plays an important role in the investigation of their distribution, temporal and spatial trends, environment fates and potential sources. Such quantitative analysis-based monitoring not only helps shareholders to share responsibility, but also provides the vital information required by regulators. However, exemptions and the loose regulation of POPs may still result in their release,