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EARLY EVALUATION OF OPFR CONTAMINATION IN ROMANIAN AQUATIC SYSTEMS

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Introduction

Organophosphate flame retardants (OPFRs) are emerging pollutants of global concern, used extensively in consumer goods, building materials, electronics, and textiles. Their persistence, bioaccumulation potential, and toxicological effects—including endocrine disruption and carcinogenicity—have raised significant concerns worldwide. Despite regulatory efforts to phase out older flame retardants, OPFRs are increasingly detected in aquatic environments, highlighting their continuous release through wastewater discharges. At the European level, environmental monitoring of OPFRs has intensified, but data remain scarce for Eastern European countries. In Romania, no previous studies have documented the occurrence, fate, or risks associated with OPFRs in urban wastewater systems. This information gap hampers the implementation of effective pollution control strategies and limits the country's alignment with EU water protection policies. The present study provides the first national-level assessment of OPFR contamination in Romania. Wastewater and surface water samples from five urban wastewater treatment plants (WWTPs) were analyzed to determine OPFR concentrations, removal efficiencies, mass flows, and ecological risks. By addressing a critical environmental knowledge gap, the study supports future regulatory action and technological improvements to mitigate OPFR pollution.

Materials and methods

Samples of influents, effluents, and surface waters were collected from five Romanian municipal WWTPs. Target analytes included eleven OPFRs: (Tri(2-chloroethyl) phosphate (TCEP), tripropyl phosphate (TPP), tri(2-chloroisopropyl) phosphate (TCPP), tri(1,3-dichloro-2-propyl) phosphate (TDCPP), tri(1,3-dibromopropyl)phosphate (TDBPP), tri(2-eylhexyl) phosphate (TMPP), triphenyl phosphate (TPHP) and the metabolites dibutyl phosphate (DBP), bi(2-ethylhexyl) phosphate (BEHP), and diphenyl phosphate (DPHP), encompassing both chlorinated and non-chlorinated species. Samples were extracted using solid-phase extraction technique. All analyses were conducted by LC-MS/MS using multiple reaction monitoring mode. Concentration data were used to compute removal efficiencies, daily mass loads and emissions per 1000 inhabitants, and risk quotients (RQ) based on existing ecotoxicological thresholds.

Results and conclusions

All eleven OPFR compounds investigated were detected in wastewater and sewage sludge samples, with the highest frequencies corresponding to chlorinated species such as TCPP, TCEP, and TDCPP. In influents, TCPP showed the highest concentrations, ranging between 1301 and 1711 ng/L, while in effluents the levels remained elevated (757÷1299 ng/L), highlighting the inefficiency of conventional treatment stages to fully eliminate these substances. The mean concentrations of non-chlorinated OPFRs (e.g., TPHP, TPP) were generally lower but still present in all treatment stages. The removal efficiency across the five monitored WWTPs was generally poor, remaining below 50% for the sum of compounds in all stations. In some cases, certain compounds such as TCEP or TDCPP showed higher concentrations in effluents than influents, suggesting transformation processes, release from sludge, or sampling variability. Among the analyzed wastewater treatment plants, the one serving the smallest population exhibited the lowest removal efficiency, whereas the plant operating in the largest urban area showed comparatively better performance, potentially due to more advanced treatment technologies or optimized operational conditions. Daily mass loading values confirmed TCPP as the major contributor to OPFRs inflow into WWTPs (up to 1364 mg/day/1000 people), followed by DBP. Corresponding daily mass emissions into receiving waters were also significant, with TCPP values reaching up to 935 mg/day/1000 people. This persistent release into natural aquatic systems raises concerns about chronic exposure of aquatic biota to OPFRs. RQ analysis revealed low ecological risks for most compounds in effluents and receiving rivers; however, moderate risk levels ($0.1 < RQ < 1$) were calculated for TCPP, TDCPP, and TMPP in certain cases, particularly for sensitive species such as algae or crustaceans. This underlines the need for targeted mitigation strategies and possible regulatory actions. In conclusion, this first national-scale monitoring effort in Romania highlights the widespread presence of OPFRs in urban wastewater systems and their incomplete removal during treatment. The discharge into natural waters require immediate attention from policymakers, especially in the context of potential human exposure and environmental risks. Future studies should address seasonal variability, treatment optimization, and the development of advanced removal techniques such as activated carbon or ozonation to mitigate OPFR pollution in the aquatic environment.