In situ partitioning of selected antibiotics in the water-sediment system: effect of pH

Aleksandër Peqini[1, 2*], Benjamin Justus Heyde[3], Ferdi Brahushi[2], Rolf-A. Düring[1]
Justus Liebig University Giessen, Giessen, Germany[1]
Agricultural University of Tirana, Tirana, Albania[2]
Ruhr University Bochum, Bochum, Germany[3]
aleksander.peqini@umwelt.uni-giessen.de

Abstract: *The presence of antibiotic residues in aquatic ecosystems has become an increasing environmental and public health concern due to their persistence, potential to disrupt microbial communities, and contribution to the development of antimicrobial resistance. These contaminants are often insufficiently removed by conventional wastewater treatment systems, allowing them to accumulate in surface waters and sediments, where they pose ecological risks. Understanding their occurrence, environmental behavior, and interactions with sediment is therefore essential for effective risk assessment and mitigation strategies. This study investigates the environmental occurrence and sediment-water partitioning behavior of the antibiotics ciprofloxacin (CFC) and clindamycin (CMC) in the Ishmi River basin, Albania. Both compounds were frequently detected in surface waters and sediments, with the highest concentrations found near urban sewage discharge points, where CFC and CMC reached up to 1.8 and 0.2 µg L^{-1} in water and 1068 and 37.8 µg kg^{-1} in sediments, respectively. Declining concentrations with decreasing urban impact were observed. The sediment-water partition coefficient (Kd) indicates high sorption tendencies for CFC and low to moderate for CMC. Partitioning behavior for CFC was influenced significantly by sediment pH, organic carbon and cations content. In case of CMC, however, organic carbon and iron (Fe) content were the main determining factors. The pH dependent n-octanol-water distribution coefficient (Dow), highlights the prominent sediment pH effect on CFC partitioning, and suggests that electrostatic interactions with negatively charged functional groups influence its environmental fate. These findings underscore the role of physicochemical interactions in controlling antibiotic distribution in sediments and highlight CFC and CMC as priority contaminants in regions with insufficient wastewater treatment.*

Keywords: *CIPROFLOXACIN; CLINDAMYCIN; SEDIMENT-WATER PARTITIONING; SEDIMENT PH; pKa; Dow*

1. Introduction

Pharmaceutical active compounds presence in the surface water bodies is becoming a challenge with the increase of world population. It is reported that in a global scale, the presence and concentration of pharmaceuticals is problematic, especially in low- to middle-income countries related with poor wastewater treatment facilities or even without any treatment technology (direct discharge) [1]. Pharmaceutical, including antibiotics pollution originates from both point sources—such as hospitals, industries, and sewage effluents—and diffuse sources like agricultural and urban runoff [2]. These pollutants enter soil and water through households, industrial and hospital effluents, landfills, animal waste, and aquaculture [2, 3]**,** as well as through irrigation with wastewater-impacted water [4]. Household discharges are the largest contributor because many pharmaceuticals are excreted unchanged [5], and their incomplete removal in conventional wastewater treatment plants makes environmental release inevitable [6, 7]. Additional sources include improper disposal of leftover medicines [5], leakage from septic systems [8], and pharmaceuticals from pets or pet waste entering household waste streams and landfills [9]. Antibiotics are widely used and in an increasing trend, both for human and veterinary use with a growing world population, even though there is a global action plan from the World Health Organization (WHO) on antimicrobial resistance which aims to reduce antibiotic use and their misuse in human, animal and agriculture [10]. These compounds negatively affect non target species as algae, bacteria and fish [11-13].

As Albania is aiming and preparing to join the European Union (EU), it has to monitor, report and to achieve a good chemical and ecological status of the water bodies, in accordance with the EU policies (Directive 2000/60/EC).

Ishmi river basin is located in the central north-west part of Albania with more than 30% of the country population living in this area (Instat Albania 2025). The area is the most important in the economic aspect with the highest industrial activity, and with no active wastewater treatment plant.

As the study area lacks wastewater treatment, thus indicating high input of CFC and CMC, therefore it is worthwhile investigating their partitioning behavior under environmental conditions. Therefore, the objective of this study was to assess the occurrence of the antibiotics CFC and CMC in water and sediments having as reference the data from consumption and assessing their partitioning behavior by considering both compound properties such as compounds K_d, K_{ow}, pK_a, $D_{ow,}$ and site-specific environmental conditions such as sediment pH, organic carbon and cations content.

2. Materials and Methods

Standards of CFC and CMC as well as internal standards, were purchased from HPC Standards GmbH (Cunnersdorf, Germany). Stock solutions of antibiotics were prepared in methanol containing 0.01% HCl. HPLC grade methanol, acetonitrile, acetone, and MilliQ water (Purelab, UK) were used throughout the study. Mettler Toledo Scale (ME 204) and pH meter (inoLab® pH 7110) were used for weighing and pH measurements.

Water and sediment samples were collected during the spring and summer seasons of the years 2023 and 2024. For water samples, glass bottles were used, while for sediments plastic containers were employed. Sampling sites were situated at established national water monitoring stations: upstream (Brari Bridge – TR1), midstream/urban areas (Casa Italia Bridge – LR1, Kamza Bridge – TR2, Rinas Bridge – IR1), and downstream (Gjoles Bridge – IR2, Salmer Bridge – IR3). TR1 represented a site with minimal anthropogenic influence. In contrast, LR1, TR2, IR1, and IR2 were heavily impacted by urban activities, particularly LR1, and with some agricultural influence IR1 and IR2. Meanwhile, IR3 was predominantly affected by agricultural activities. Water samples were filtered using 0.45 µm cellulose acetate filters, pH was adjusted to around 2.7, internal standards were added and measured via HPLC-MS/MS based on the reported method [14]. Sediment samples were collected at 0–5 cm depth, immediately cooled, then frozen at -28 °C and subsequently lyophilized. Dried sediments were sieved to <100 µm, characterized, and analyzed for CFC and CMC based on reported validated method [14].

The sediment–water partition coefficient (K_d) for CFC and CMC was calculated using their concentrations in the sediment phase (C_s) (ng g^{-1}) and the water phase (C_w) (ng L^{-1}), as given below:

$$K_d = C_s / C_w$$

Meanwhile, the distribution behavior of the selected pharmaceuticals D_{ow} was calculated as given below:

$$D_{ow} = \frac{K_{ow}}{1+(10^{pH-pK_a})}$$

3. Results and Discussion

A two-year (2023-2024) assessment was realized, and the study focus compounds were detected with (average values) 0.18 – 0.71 µg L^{-1} and 3.2 - 705 µg kg^{-1} for CFC, and 0.005 - 0.04 µg L^{-1} and 3.8 – 17.8 µg kg^{-1} for CMC, in water and sediments, respectively for the two years (Fig. 2). These results are in line and reflect the consumed amounts (only the Albanian state reimbursed amounts, which could represent only 1 % of total consumed amounts of the two compounds in Albania) of CFC with 7.2 and 6.7 kg, and CMC with 0.0 kg, respectively for the two years (Fig. 1).

The effect of pH is one of the most important vital factors in the sorption process due to the impact and the control of the sediment charge and speciation of the compounds, in this case of CFC and CMC due to their anionic properties [15]. CFC has two pK_a values of 6.09 and 8.76, and within the relevant pH (6.4-8.4) can be mainly zwitterionic but at the same time, can be charged positively, negatively, or uncharged. CMC has a pK_a of 7.6 in the pH range (6.4-8.4) (Fig. 3) of the studied sediments, existed predominantly in its cationic form (CMC^+) at pH values under 7.6, and mostly in its neutral form (CMC^0) at pH values above 7.6.

As sediment pH increases, the net negative charge of the sediment also increases, due to the deprotonation of surface functional groups (–OH) [16].

Therefore, the sediment CFC uptake mechanism is through electrostatic interactions between cationic CFC^+ with sediment surface negatively charged sediment functional groups, such as –OH, –COOH (supported with the positive linear correlation of CFC K_d with the organic carbon content, $p < 0.05$) (Fig. 3), C–O, and Si–O–Si. This is supported by the fact that the detected CFC concentrations in sediments are like the percentage of CFC^+, and a significant negative correlation of CFC K_d with sediment pH and D_{ow} (Fig. 3 and Fig. 6). CFC K_d showed negative correlation with Ca, Mg, K, and Fe; thus these cations act as neutralizing agents' sediment negative charges, resulting in an inhibitory effect on CFC sorption and Fe only for (CMC).

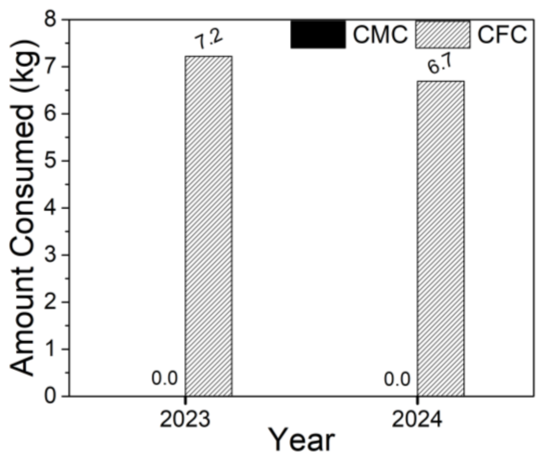


Fig. 1 Amounts of consumed CFC and CMC for the years 2023 and 2024 in Albania (only state reimbursed amounts)[17]

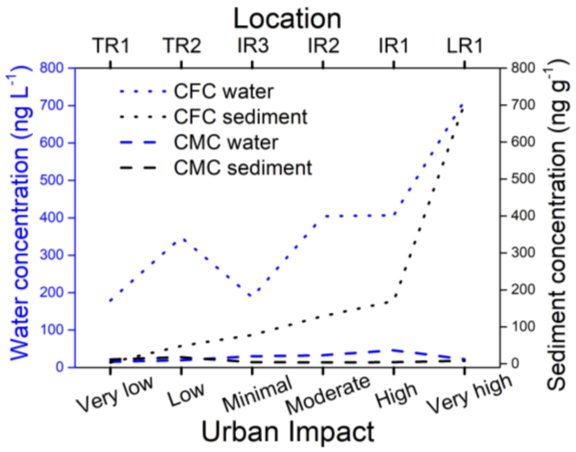


***Fig. 2** Concentrations of CFC and CMC in Ishmi river basin for the years 2023 and 2024*

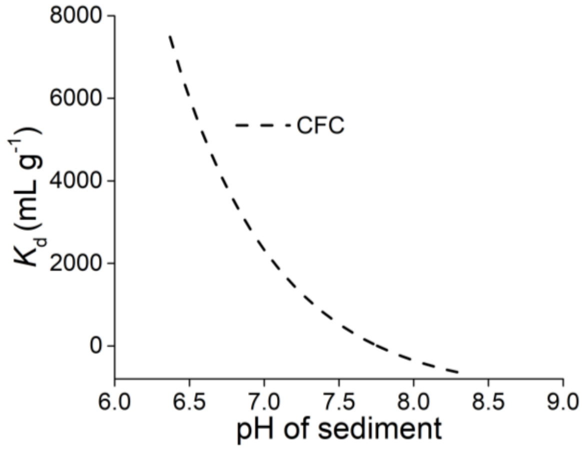


***Fig. 3** The effect of sediment pH on CFC K_d*

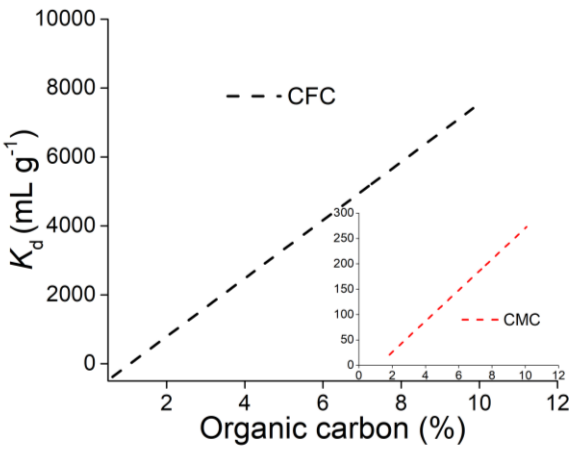
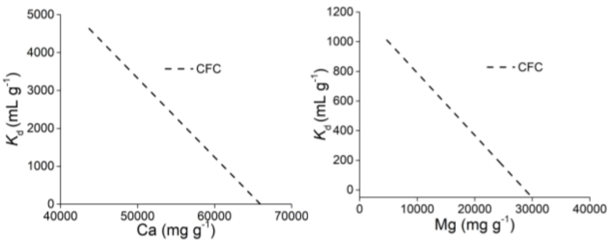


***Fig. 4** The effect of sediment organic carbon content on CFC and CMC K_d*



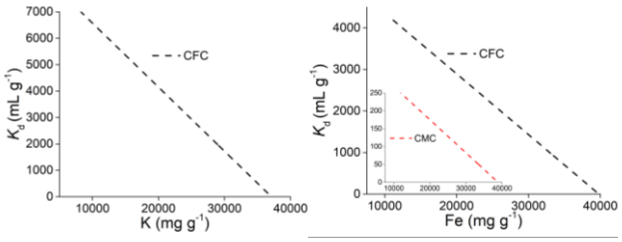


Fig. 5 *The effect of sediment cations content on CFC (Ca, Mg, and K had significant effect) and CMC (only Fe had significant effect) K_d*

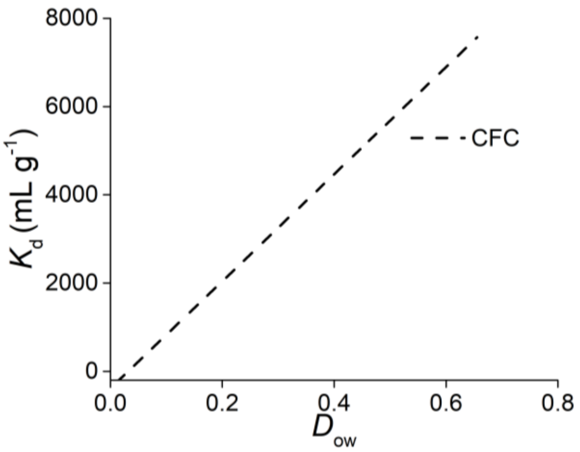


Fig. 6 *The relationship between CFC K_d with the pH dependent n-octanol-water distribution coefficient (D_{ow})*

4. Conclusions

Overall, CFC levels were detected at higher concentrations in both water and sediment compared to CMC, indicating their greater persistence and mobility within the riverine system. In contrast, CMC appeared at substantially lower levels. These results are in accordance with the data from mandatory health insurance fund of Albania where CFC was reported in higher consumed amounts, meanwhile CMC was reported as non-consumed amounts.

The partitioning behavior of CFC in the sediment–water interface was strongly and significantly controlled by pH (D_{ow}), organic carbon, and major cations such as Ca, Mg, K, and Na. Meanwhile, CMC distribution was primarily influenced by organic carbon and Fe content. These findings highlight the important role of sediment geochemistry and water chemistry in governing the environmental fate of pharmaceuticals and underscore the need to consider site-specific physicochemical characteristics when assessing their transport and potential ecological risks.

5. References

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