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The effects of natural and anthropogenic inputs on boron isotopes in the Han River basin

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Boron (B), a micronutrient and highly soluble element, exhibits significant sensitivity to biogeochemical processes, making its concentration and isotopic composition ($\delta^{11}B$) valuable tracers in environmental studies. This study investigated the coupled elemental and boron isotopic geochemistry of river waters and wastewaters within the Han River basin during the high flood season to disentangle the influence of natural and anthropogenic processes on riverine B dynamics. Two distinct tributaries displayed contrasting elemental characteristics: the Bukhan River (BHR), draining crystalline bedrock, exhibited substantially lower B concentrations compared to the Namhan River (NHR), which traverses sedimentary formations. This disparity suggests a dominant control of sediment weathering on riverine B concentration, although potential anthropogenic contributions induced from positive correlation between B and Cl were not discounted. Following the confluence of these tributaries at the Paldang Dam, the main Han River (MHR) showed increased elemental concentrations downstream of the Seoul metropolitan area, indicative of anthropogenic inputs. Conversely, despite notable lithological differences, the tributaries exhibited similar $\delta^{11}B$ values (BHR: +15.8‰; NHR: +13.4‰), significantly enriched relative to their respective bedrocks. This B isotopic enrichment suggests a strong influence of secondary phase formation and potentially plant uptake on riverine B isotope signatures. Intriguingly, the MHR maintained $\delta^{11}B$ values consistent with the two tributaries, displaying minimal downstream variation. This constancy suggests either an isotopically indistinguishable anthropogenic B input or a negligible anthropogenic impact on the bulk riverine B isotope composition due to much higher discharge of the MHR compared to wastewater input. While wastewater $\delta^{11}B$ values largely overlapped with river water, with the exception of one outlier, the data suggest that anthropogenic B inputs in the MHR are likely masked by the river's pre-existing isotopic signature. In short, our findings indicate that B isotopes in the major Han River tributaries are primarily governed by silicate weathering and subsequent clay neoformation, irrespective of lithology, with localized wastewater impacts in the MHR. Critically, this study highlights the importance of cautious interpretation of B isotope data in tracing anthropogenic inputs because wastewater treatment can effectively minimize the $\delta^{11}B$ contrast between river water and wastewater.