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Comparison of the elemental composition of different hard parts (otoliths, scales, fin rays, vertebrae and eye lenses) of freshwater fish using ICPMS

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Elemental and isotopic fingerprints of different hard parts of fish are a powerful tool to gain life history information of individual fish. Most of these structures, like otoliths, scales, fin rays and vertebrae show incremental growth, allowing for a time resolved analysis of this information using e.g. laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). Scales and fin-rays serve as important non-lethal alternatives to otoliths. Additional structures without incremental growth such as eye lenses might contain complementary information. However, there is a lack of solid matrix-matched reference materials that are needed to quantify elemental concentrations using LA-ICPMS. In this study we determined the elemental composition ("elemental fingerprint") of otoliths, scales, fin rays, vertebrae and eye lenses from freshwater fish of the Danube catchment using microwave-assisted digestion and solution based inductively coupled plasma mass spectrometry in order to gain information on the natural concentration ranges of various elements of interest in such samples. The investigation has focused on macro (Ca, Mg and P), minor and trace elements (Ba, Cu, Mn, Pb, Sr and Zn). Method validation was performed using the following certified reference materials (CRMs): riverine water (NRC SLRS-5), bone ash (NIST SRM 1400), bone meal (NIST SRM 1486) and fish otolith (NRC FEBS-1). Significant differences in elemental concentrations among different hard parts analyzed were found suggesting that different structures might be suited for a particular research purpose e.g. tracing environmental pollution. Based on this work, the preparation of in-house certified matrix-matched reference materials (co-precipitated hydroxyapatite calibration standards pressed to pellets) is established allowing for the quantification of the elemental concentration on a time resolved level in different hard parts by direct solid sampling via laser.