SM1. Organic compounds - Analytical procedures

The analytical procedure for the organic compounds (AHs, PAHs, n-alcohols and sterols) analysis was similar to that reported by Lourenço et al. (2021). Twenty grams of freeze-dried sediment were 8-h Soxhlet extracted with 80 ml of dichloromethane-hexane (1:1, v:v). The surrogates 5α-androstanol (for sterols and n-alcohols), naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (for PAH), and 1-hexadecene and 1-eicosene (for AHs) were added prior extraction to each sample. The concentrated extracts (1 ml) were introduced to an adsorption chromatography column with 2 g of 95% activated alumina. Elution was performed using 10 ml of a mixture (3:7) of n-hexane:dichloromethane (fraction 1 – AH and PAH) and 15 ml of (1:1) n-hexane:methanol (fraction 2 – n-alcohols and sterols). The extracts from fraction 1, AH and PAH, were concentrated to 0.5 ml. The extracts from fraction 2, n-alcohols and sterols, were evaporated to dryness and derivatized to form trimethylsilyl ethers using 40µl of bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) for 90 min at 65 °C. After BSTFA/TCMS was evaporated to dryness, and fraction 2 was recovered in n-hexane (0.5 ml). Internal standards, 1-tetradecene (AH), p-terphenyl-d_{14} (PAH), and 5α-cholestane (n-alcohols and sterols), were added before chromatographic analyses. N-alkanes (from n-$C_{10}$to n-C_{40}), pristane, and phytane analyses were performed using an Agilent GC (model 6890) equipped with a flame ionization detector (FID) and an HP-5 fused silica column (Agilent 19091J-015, 50 m length, 0.32 mm ID, and 0.17 µm film thickness). Hydrogen was used as the carrier gas. The injector temperature was adjusted to 300 °C, and splitless injection was adopted. The oven temperature was programmed to start at 40 °C and hold for 1.5 min and then increase to 325 °C at 10 °C min^{-1}, holding at 325 °C for 10 min. The PAH analyses were performed using an Agilent GC model 6890N coupled to an Agilent single quadrupole (MS) model 5973N equipped with HP5-MS capillary fused silica column (Agilent 19091S-433, 30 m length, 0.25 mm ID, 0.25 µm film thickness). Helium was used as a carrier gas. The injector temperature was adjusted to 300 °C, and splitless injection was adopted. The oven temperature was programmed to start at 40 °C and hold for 2 min, from 40 to 100 °C at 25 °C min^{-1}, from 100 to 230 °C at 5 °C min^{-1}, from 230 to 270 °C at 2 °C min^{-1} holding at 270 °C for 5 min, and finally to 300 °C at 5 °C min^{-1}. Sterols and n-alcohols analyses were performed using an Agilent gas chromatograph (GC) model 7890B coupled to an Agilent triple-quadrupole (TQMS - model 7010B). Separations were achieved with an HP5-MS capillary fused silica column (Agilent 19091S-433UI, 30 m length, 0.25 mm ID, 0.25 µm film thickness). Helium was used as the carrier gas. The oven temperature was programmed from 40 to 240 °C at 10 °C min^{-1}, then 245 °C at 1.0 °C min^{-1}(holding for 5 min), and finally 300 °C at 4°C min^{-1} (holding for 5 min). The injector temperature was adjusted to 300 °C, and splitless injection was adopted. Compounds were identified by matching the retention times with the results from standard compounds and by the ion mass fragments (m/z) when GC-TQMS and GC-MS were adopted. Individual compound concentrations were obtained using the surrogate standard peaks area method and 5-point analytical curves for individual components. Procedural blanks (calcined Na_2SO_4)

analyses were performed at the same extraction batch of the samples, and no peaks interfered with the analyses of the target compounds. The recoveries of the surrogates, considering all samples and all classes of compounds, ranged from 70 to 105%. A spike-recovery experiment (spiked blank and spiked sediment sample) was conducted during the extraction of the samples, and the recoveries of the spiked compounds, of all classes of compounds, ranged from 63 to 98%. Detection limits (DL) calculated, in dry weight, were 1.0 ng $g^{-1}$for AH, 0.12 ng $g^{-1}$for PAH, and 10 ng $g^{-1}$for sterols.