Organic matter, geochemical and colorimetric properties of potential source material, target sediment and laboratory mixtures for conducting sediment fingerprinting approaches in the Mano Dam Reservoir (Hayama Lake) catchment, Fukushima Prefecture, Japan.

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1. Introduction

A Thematic School was organised in October 2021 (https://www.lsce.ipsl.fr/tracing2021/) to come up with concrete suggestions to improve the design and implementation of sediment fingerprinting or tracing methods. Among these, best practices to share tracing data and samples, which will increase the visibility of the fingerprinting technique in geoscience, are to be promoted (Evrard et al., 2022). The current dataset proposes sediment tracing data along with the associated metadata for potential source and target material samples registered using the SESAR website (https://www.geosamples.org/) to attribute each sample with an International Geological Sample Number (IGSN). The current dataset may provide a template for colleagues from the international scientific community dealing with sediment fingerprinting to share their own data.

The current dataset was compiled to investigate the redistribution of sediment contaminated with radionuclides emitted following the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident that occurred in March 2011 in Northeastern Japan (Evrard et al., 2015; Onda et al., 2020). The radioactive plume is drained by several coastal rivers to the Pacific Ocean, and sediment-bound radionuclide transfers in these rivers are mainly controlled by the occurrence of typhoons and tropical storms (Evrard et al., 2021). The dataset was mainly produced to understand the changes in land use-based source contributions to sediment with time in the Mano Dam Reservoir, also referred to as Hayama Lake, before and after FDNPP accident. To this end, a sediment core was collected in the lower part of the reservoir in June 2021. As such, this dataset represents an

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extension of previous work conducted on sediment cores collected in the same reservoir in 2014, i.e. early after the nuclear accident (Huon et al., 2018).

The current dataset comprises three Excel files including the metadata description, the data itself and a file describing the composition of laboratory mixtures prepared to provide a dataset to calibrate/validate un-mixing models implemented to address this research question and analysed in the same conditions and using the same equipment as the source/target material (Batista et al., 2022).

2. Materials and Methods

2.1. Organic matter and stable isotopes

In the Hayama lake catchment, sediment and soils were found not to contain carbonate minerals, and all the carbon associated with particulate matter is organic in nature (Huon et al., 2018). Total organic carbon (TOC) and total nitrogen (TN) elemental concentrations and isotopes (δ^{13}C and δ^{15}N) were determined by a combustion method using a continuous flow elementary analyser (Elementar VarioPyro cube) coupled with an Isotope Ratio Mass Spectrometer (EA-IRMS) (Micromass Isoprime) at the Institute of Ecology and Environmental Sciences (iEES Paris) in France. A first analysis run was conducted to measure TOC concentration together with a set of tyrosine standards (Coplen et al., 1983). The second analysis run was dedicated to measure TN concentration after sample weight optimisation from TOC results. For combustion, oxygen was injected during 70 s (30 mL.min^{-1}) at 850 $^\circ C$ for reduction and the combustion furnace at 1120 $^\circ C$ (Agnihotri et al., 2014). The analytical precision was assessed with repeated analyses of a tyrosine intern standard ($n = 51$), calibrated against international reference standards (Girardin & Mariotti, 1991). The uncertainties associated with the calculation of TOC/TN and TN/TOC ratio were calculated with the ratio uncertainty propagation function (eq. 8). The soil source measurements were described in the study of Laceby et al. (2016). To evaluate the nature of sedimentary organic matter, terrestrial and/or freshwater, the distribution of sample values was plotted in a δ^{13}C (d13C_PrM) vers. TOC/TN diagram and compared to the thresholds reported in Lamb et al. (2006) thresholds.

2.2. Geochemistry

Elemental geochemistry was determined using X-ray fluorescence (XRF) (Malvern Panalytical, ED-XRF Epsilon 4). A total of 15 elemental concentrations were measured (Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Rb, Si, Sr, Ti, Zn, and Zr). Measurements were conducted in containers covered with a 3.6 μm thin Mylar film (Chemplex, Mylar Thin-Film cat. no. 157) with a 10 mm exposure surface. A minimum of 0.1 g of material was analysed. To consider the potential heterogeneity within a sample, three replicate measurements were made, and the mean value was calculated. To assess the accuracy of the measurement, a standard (JMS-1, sediment from the Tokyo Bay (Terashima et al., 2007)) was measured every seven samples ($n = 38$) and the accuracy of the measured batch was determined with the calculation of the Root Mean Square Errors (RMSE).

2.3. Visible colorimetry

Visible colorimetry was measured using a portable diffuse reflectance spectrophotometer, Kanonica Minolta CM-700d, set on a 3 mm target radius. Samples were measured in a plastic zip bag. In order to take into account potential heterogeneity within a sample, three measurements were made at different locations on the bag. The spectrophotometer was calibrated at the start of each set of measurements with a zero (black) and white standards. Measurements were conducted according to the D65 illuminance standard, 10° angle observer and excluding the specular component. The spectral reflectance (in %) was measured from 360 nm to 740 nm with a 10 nm resolution (30 wavelength classes). Raw data was processed using the colour data software CM-S100w SpectraMagic NX (Kanonica Minolta, 2022). Colour parameters within the Cartesian coordinate systems CIE Lab (1976) (i.e. L*, a* and b*) (ISO 11664-4:2008) and CIE LCh (i.e. C* and h) were exported. The CIE LCh is a vector representation of the CIE Lab (1976), where vectors are calculated as follows:

$$C^* = \sqrt{a^{*2} + b^{*2}}, \tag{1}$$

$$h = \begin{cases} \arctan(b^*/a^*) & \text{if } \arctan(b^*/a^*) \geqslant 0 \\ \arctan(b^*/a^*) + 360 & \text{otherwise} \end{cases} \tag{2}$$

Within the CIE Lab system: L* is the lightness of the colour, from black (0) to white (100), a* is the position between green to red (negative values are associated with green and positives with red), b* is the position between blue and yellow (negative values are associated with blue and positive values with yellow). Within the CIE LCh system: C* is the chroma (positive values are associated to brighter colors and negative values to duller colors) and h is the hue angle (in °) in the CIE Lab color wheel.

The Q7/4 ratio as defined by Debret et al. (2011) was calculated as the ratio between 700 nm and 400 nm reflectance values, its uncertainty was calculated with equation 4.

The oxy-hydroxide geothite ($\alpha - \text{FeOOH}$) peaks at 445 nm and 525 nm as defined by Debret et al. (2011) were calculated from the first derivative reflectance spectra. For each replicate of the measurement and for each sample, the first derivative reflectance spectra was calculated and smoothed with a Savitzky-Golay filter using the savitzkyGolay function (differentiation order = 1, polynomial order = 3, window size = 5) from R package prospectr (Stevens & Ramirez-Lopez, 2022, ver. 0.2.5) then the mean per sample and the standard deviation were calculated. From the first derivative of reflectance, two geothite peaks were calculated: first, the 445 nm peak value was calculated as the mean of values at 440 and 450 nm, and the 525 nm peak as the mean of those at 520 and 530 nm. The uncertainty associated with these peaks was calculated with equation 5.

The remission function was calculated from the reflectance spectra: $f(R) = (1 - R)^2$ according to the Kubelka-Munk relationship (Scheinost et al., 1998). Then, the second derivative was calculated and the spectra was smoothed with a Savitzky-Golay filter using the savitzkyGolay function (differentiation order = 2, polynomial order = 3, window size = 5). From the second derivative of remission function spectra, the iron oxide-associated parameters A1, A2, A3 and the goethite

proportion within iron oxides (Gt) were calculated following the approach defined by Tiecher et al. (2015). The peaks A1 and A2 are associated with goethite and A3 with hematite and were calculated as the amplitude between each maximum and minimum bands. Thus A1 is the difference between 450 and 420 nm, A2 is the difference of 510 and 480 nm and A3 is the difference of 575 (as the mean of 570 and 580 nm) and 535 nm (as the mean of 530 and 540 nm) and Gt as the ratio of A1/(A1+A3). The uncertainty associated with A1 and A2 were calculated with equation 6, A3 uncertainty and Gt uncertainty were calculated with equation 7 and equation 8, respectively.

2.4. Uncertainty propagation formulas

Uncertainty (ΔR) was calculated using a propagation of uncertainty equation, with f a set of non-linear combinations of the variables x, with the Taylor expansion being:

$$\Delta R = \sqrt{\sum_{i=1}^{n} \frac{\partial f_i}{\partial x_i} \cdot x_i}, \tag{3}$$

Then, for the calculations conducted in the current research following uncertainty propagation formulas were developed from the Taylor expansion. In theses formulas the following notation referring to A as an analysis (e.g. TOC) and ΔA as its error (e.g. TOC_SD) was used.

Uncertainty Propagation formula for a division:

$$\Delta\left(\frac{A}{B}\right) = \sqrt{\left(\frac{1}{B} \cdot \Delta A\right)^2 + \left(-\frac{A}{B^2} \cdot \Delta B\right)^2}, \tag{4}$$

Uncertainty Propagation formula for the mean of two values:

$$\Delta\left(\frac{A+B}{2}\right) = \sqrt{\left(\frac{1}{2} \cdot \Delta A\right)^2 + \left(-\frac{1}{2} \cdot \Delta B\right)^2}, \tag{5}$$

Uncertainty Propagation formula for a difference:

$$\Delta(A - B) = \sqrt{(\Delta A)^2 + (-\Delta B)^2}, \tag{6}$$

Uncertainty Propagation formula for a difference of means:

$$\Delta\left(\frac{A+B}{2} - \frac{C+D}{2}\right) = \sqrt{\left(\frac{1}{2} \cdot \Delta A\right)^2 + \left(\frac{1}{2} \cdot \Delta B\right)^2 + \left(-\frac{1}{2} \cdot \Delta C\right)^2 + \left(-\frac{1}{2} \cdot \Delta D\right)^2}, \tag{7}$$

Propagation of uncertainty for a proportion:

$$\Delta\left(\frac{A}{A+B}\right) = \sqrt{\left(\frac{B}{(A+B)^2} \cdot \Delta A\right)^2 + \left(-\frac{A}{(A+B)^2} \cdot \Delta B\right)^2}, \tag{8}$$

All processing was achieved using R programming environment (R Core Team, 2021, ver. 4.1.0) within RStudio (RStudio Team, 2022, ver. 2022.7.1.554).

2.5. Mapping

Lithological and pedological classifications of soil samples were obtained through location-based extraction from the Fukushima 1:200.000 geological map (Kubo et al., 2003) and the 1:50.000 pedological map (NARO, 2011), respectively. Soil pedologic classes correspond to the English translations of Japanese soil type names according to the Comprehensive Soil Classification System of Japan (Obara et al., 2011). All map processing was conducted in QGIS (QGIS Development Team, 2022, ver 3.26.0).

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