From Canals to the Coast: Dissolved Organic Matter and Trace Metal Composition in Rivers Draining Degraded Tropical Peatlands in Indonesia

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Abstract. Worldwide, peatlands are important sources of dissolved organic matter (DOM) and trace metals (TM) to surface waters and these fluxes may increase with peatland degradation. In Southeast Asia, tropical peatlands are being rapidly deforested and drained. The black rivers draining these peatland areas have high concentrations of DOM, and the potential to be hotspots for CO_2 release. However, the fate of this fluvial carbon export is uncertain, and its role as a trace metal carrier has never been investigated. This work aims to address these gaps in our understanding of tropical peatland DOM and associated elements in the context of degraded tropical peatlands in Indonesian Borneo. We quantified dissolved organic carbon and trace metal concentrations in the dissolved and fine colloidal (<0.22µm) and coarse colloidal (0.22 – 2.7 µm) fractions and determined the characteristics ($\delta^{13}C$, Absorbance, Fluorescence: excitation-emission matrix and PARAFAC analysis) of the peatland-derived DOM as it drains from peatland canals, flows along the Ambawang River, a black river, and eventually mixes with the Kapuas Kecil River (white river) before meeting the ocean near the city of Pontianak in West Kalimantan, Indonesia. We observe downstream shifts in indicators of in-stream processing. An increase in the $\delta^{13}C$ of DOC, along with an increase in the C1/C2 ratio of PARAFAC fluorophores, and decrease in SUVA (Specific UV Absorbance) along the continuum suggest the predominance of photo-oxidation. However, very low dissolved oxygen concentrations also suggest that oxygen is quickly consumed by microbial degradation of DOM in the shallow layers of water. Black rivers draining degraded peatlands show significantly higher concentrations of Al, Fe, Pb, As, Ni, and Cd, compared the white river. A strong association is observed between DOM, Fe, As, Cd and Zn in the dissolved and fine colloid fraction, while Al is associated with Pb and Ni and present in a higher proportion in the coarse colloidal fraction. We additionally measured the isotopic composition of lead released from degraded tropical peatlands for the first time and show that Pb originates from anthropogenic atmospheric

deposition. Degraded tropical peatlands are important sources of DOM and trace metals to rivers and a secondary source of atmospherically deposited contaminants.

Keywords: Tropical peatlands, Dissolved Organic Matter, Absorbance, Fluorescence, PARAFAC, Stable isotopes, Trace metal, Lead isotopes

1. Introduction

Most Southeast Asian tropical peatlands developed as domes beneath ombrotrophic peat swamp forests (Page et al., 2006; Cobb et al. 2017). They store at least 68.5 Pg C, or 15-19% of the global peat carbon stocks (Dargie et al., 2017; Lähteenoja et al., 2009; Page et al., 2011). They have experienced widespread degradation as a result of deforestation, conversion to agriculture and drainage, which all accelerated in the late 2000s. This abrupt change in land use, and corresponding lowering of the water table, has led to subsidence and a massive release of carbon from peatlands to the atmosphere due to enhanced aerobic decomposition of organic matter from the drained peat. Extensive work has focused on quantifying the resulting CO_2 fluxes (Couwenberg et al., 2010; Hoyt et al., 2019; Jauhiainen et al., 2012; Miettinen et al., 2017) and land surface subsidence (e.g. Hooijer et al., 2012; Carlson et al., 2015).

Drainage canals are dug in forested peatlands for multiple reasons: first, as a mechanism to transport timber out of the peatland during deforestation, and later to lower the water table, making the land suitable for agriculture. These peatland drainage canals channel water from the peatlands to surrounding surface waters. The resulting fluvial export of dissolved organic matter (DOM) has been recognized as an important component of the carbon budget of tropical peatlands, that could increase with deforestation and peatland exploitation (Gandois et al., 2013; Moore et al., 2011). Indonesia alone contributes over 10% of the global riverine dissolved organic carbon (DOC) input into the ocean (Baum et al., 2007), as a result of both high peatland coverage and high precipitation rates. This proportion is likely to increase with rapid peatland conversion to agriculture, which destabilizes long-term peat C stocks (Moore et al., 2013).

Another implication of DOM transfers from peatlands to surface water is the transport of associated elements, especially trace metals (TM). Tropical peatlands in Southeast Asia are mainly ombrotrophic systems, which receive critical nutrients through atmospheric deposition, and serve as a sink for atmospheric pollutants (Weiss et al., 2002). Northern peatlands have been shown to constitute a source of major and trace elements to surface waters (Broder and Biester, 2017; Jeremiason et al., 2018; Rothwell et al., 2007). This has important implications: as a result of colloidal association between peatland-derived organic molecules and Fe, northern peatlands are responsible for a significant transfer of Fe to the Atlantic Ocean (Krachler et al. 2010, 2012). In the UK, peat degradation and erosion has led to the dispersion of lead into watersheds, which previously accumulated through atmospheric deposition over decades (Rothwell et al., 2008). Although drainage of tropical peatlands is occurring at a rapid rate across Southeast Asia, to our knowledge no data are available on trace metal release in black rivers draining tropical peatlands.

Black rivers draining peatlands (as defined in Alkhatib et al., (2007)) also have the potential to be hotspots of fluvial carbon degassing (Müller et al., 2015; Wit et al., 2015). By measuring pCO_2 in Indonesian and Malaysian

black rivers, Wit et al. (2015) estimated that 53% of DOC entering surface waters was converted to CO_2, which is similar to global averages for inland waters. In contrast, black river measurements and incubations by Martin et al., (2018) found a smaller proportion of DOC was processed in rivers. Rixen et al., (2008) also found a large proportion of the DOM was resistant to decomposition in a laboratory incubation study. These studies have focused on CO_2 measurements and incubations to assess the potential for DOM processing.

Monitoring both isotopic and optical characteristics of DOM composition in canals and rivers can provide complementary information on the extent of in-stream processing of fluvial carbon, and potential emission of greenhouse gases (GHGs) to the atmosphere. Qualitative evaluation of in-stream DOM transformation by UV light and microbial processes can be performed using isotopic and optical characterization of DOM. The stable isotope signature of DOM is both an indicator of its origin (Barber et al., 2017; Hood et al., 2005), as well as transformation processes. Lalonde et al. (2014) assessed photochemical processing of DOM in major rivers worldwide, and found that it caused an increase in the $\delta^{13}C$ of DOM of 0.5 to 2.3‰. Similarly, microbial processing is also expected to lead to an increase in the $\delta^{13}C$ of DOM. Optical properties of DOM are also sensitive indicators of DOM processing (Hansen et al., 2016; Harun et al., 2015; Spencer et al., 2009). However, in contrast to the $\delta^{13}C$ of DOM, which is similarly enriched by both microbial processing and photo-oxidation, the optical properties of DOM change in opposite directions in response to microbial processing or photo-oxidation. Microbial processing is generally found to increase the aromaticity of DOM by selective processing of less aromatic molecules, while photo-oxidation tends to decrease aromaticity, because of selective photo-oxidation of aromatic moieties (Spencer et al., 2009; Hansen et al., 2016).

In summary, although there has been an increase in efforts to quantify DOC exports from tropical peatlands, our complementary understanding of the transfer of associated elements and in-stream processing of DOM remains limited. This work aims to address these gaps in our understanding of the composition and evolution of tropical peatland DOM and how it could act as a carrier of trace metals to surface waters, in the context of highly degraded tropical peatlands in Indonesia. We characterize the quality of the peatland-derived DOM and trace metals as they drain from peatland canals, flow along black rivers, and eventually mix with a white water river before meeting the ocean. We assess spatial and seasonal changes in the organic matter quality, and document changes in DOM composition due to transport, mixing, and processing. We also assess black river trace metal release to surface waters, analyzing trace metal concentrations and the isotopic composition of lead released from degraded tropical peatlands for the first time.

2. Material and methods

2.1 Study area

The study area is located in West Kalimantan, Indonesia, near the city of Pontianak (0.09°N, 109.24°E) on the island of Borneo (Figure 1). The climate is humid equatorial with 2953±564 mm of rainfall and a mean annual temperature of 27°C (1985-2017 data). The monthly annual rainfall ranges from 170±126 mm (August) to 349±98 mm (November). The highest rainfalls are measured from October to January. The mean rainfall is 274 ± 123 mm for January, and 199 ± 106 mm for June. (Figure SI.1). The study focused on the Ambawang River, which flows into the Landak river, which in turn flows into Kapuas Kecil river. It is a black river draining a watershed

(approximatively 706 km^2) entirely covered with peatlands. This river was selected to represent water of exclusively peatland origin. All peatlands in the sampling area have been drained and converted to agriculture. Current land use consists of small scale rubber plantation, secondary forest, oil palm plantation, and human settlements.

2.2 Sample collection and treatment

Two sampling campaigns were conducted in June 2013 (drier period) and January 2014 (wetter period). Using a boat, samples were collected in the center of the river, from the origin of the Ambawang river (BR, black river sites) to its downstream confluence with the Landak and Kapuas Kecil Kecil (WR, white river sites). White river samples collected upstream of the confluence with the white river (WRu, white river upstream). Drainage canals (DC) flowing into the black river were also sampled during the second sampling campaign (Figure 1). In January 2014, a rain collector was installed on the roof of the Pontianak's meteorological station to collect rain samples for lead isotopic analysis. In situ parameters (pH, conductivity and dissolved oxygen) were measured using a multiparameter probe (WTW, Germany). Depth profiles of dissolved oxygen in the black river were also measured with an oxygen microelectrode (MI-730 dip-type micro-oxygen electrode and O2-ADPT adapter; Microelectrodes, Inc., Bedford, NH, USA). Frequent calibration was performed with a zero oxygen solution and distilled water equilibrated to ambient oxygen concentrations, where temperature was carefully monitored. To create the zero oxygen solution, 1 g of sodium sulfite (Na_2S0_3) and a few crystals (~1 mg) of cobalt chloride ($CoC1_2$) was dissolved in 1 L of distilled water. For measurements of additional parameters, a larger volume of water was collected for further analysis. Samples were filtered immediately following collection on the boat using a portable peristaltic pump (Geotech, USA) and prebaked (5h, 450°C) and pre-weighed GF/F filters (0.7 µm) and stored in glass bottles for DOC, δ^{13}C-DOC and optical properties of DOM analysis, and acidified with HCl for DOC and δ^{13}C-DOC. Samples were filtered with cellulose acetate filters (0.22 µm), acidified with HNO_3 and stored in polypropylene vials for analysis of major nutrients and trace element. DOC analysis was repeated on the cellulose acetate samples and DOC concentrations did not differ significantly based on filtration at 0.2 or 0.7 µm. In January 2014, at selected sites (8), samples were first filtered with GF/D filters (2.7µm) to assess to the coarse colloidal fraction of trace metals and DOC.

3. Sample analysis

Non-purgeable organic carbon (NPOC, referred to hereafter as DOC) was analyzed on filtered (GF/F Whatman) samples after acidification to pH 2 (HCl) with a TOC-V CSH analyzer (Shimadzu, Japan), with a quantification limit of 1 mg L^{-1}. Major cations and anions were analysed using an HPLC (Dionex, USA). The quantification limit was 0.5 mg L^{-1} for chloride, nitrate and sulphates and 0.025 mg L^{-1} for ammonium, potassium, magnesium and calcium. Certified material (ion 915 and ion 96.4 Environment and Climate Change Canada, Canada) was included in the analytical loop and recovery was >95% of the certified value. For trace element analysis, samples were acidified with ultrapure HNO_3 prior to ICP-MS (7500 ce, Agilent Technologies) analysis. ^{115}In was used as an internal standard, and SLRS-4 (River water certified for trace elements) was used as a reference material on every run and accuracy (recovery>95%) was checked. Determination limits were < 0.5 µg g^{-1} for Fe and Al, <0.05 µg g^{-1} for Ni, Cu and Zn and < 0.005 µg g^{-1} for Cd and Pb. Pb isotope ratios (^{206}Pb/^{207}Pb; ^{208}Pb/^{206}Pb) in water samples

were analyzed using a High Resolution ICP-MS (Thermo Element II XR; OMP service ICP-MS, Toulouse, France). Measurements were corrected for mass bias using individual sample bracketing with certified and adequately diluted NIST NBS-981 (100 ng L^{-1} to 500 ng L^{-1}) according to Krachler et al. (2004).

The UV absorption spectra of pore water were measured with a spectrophotometer (Secoman UVi-lightXT5) from 190 to 700 nm in a 1 cm quartz cell. The Specific UV Absorbance at 254 nm (SUVA, L mg^{-1} m^{-1}) was calculated as follows: SUVA= A_{254}/(b*DOC) (Weishaar et al., 2003), where A_{254} is the sample absorbance at 254 nm (non-dimensional), b is the optical path length (m) and DOC is in mg L^{-1}. The baseline was determined with ultra-pure water. Potential additional absorbance related to Fe content was following the procedure described by Poulin et al., (2014). The additional absorbance was small, and represented only 3.6 ± 1.4% of the total absorbance across all samples and was therefore neglected.

Emission Excitation Matrices (EEM) were acquired using a Hitachi F4500 fluorescence spectrometer, and instrument specific correction were applied. Emission spectra were acquired from 250 to 550 nm for excitation ranging from 250 to 550 nm. The slits were set to 5 nm for both the excitation and emission monochromators. The scan speed was 2400 nm min^{-1} and the integration response was 0.1 s. Fluorescence intensity was corrected from the excitation beam to ensure stability. The inner filter effect water was taken into account using a dilution approach as developed by Luciani et al. (2009). The fluorescence index was calculated as defined by McKnight et al. (2001) and Jaffé et al. (2008), by the ratio of the fluorescence intensity at 470 nm to the fluorescence intensity at 520 nm for a 370 nm excitation. The shape of the excitation spectra was checked following the recommendation of Cory et al., (2010). The PARAFAC analysis (PARAllel FACtor analysis (Bro, 1997)) was performed on all samples using the PROGMEEF program in Matlab (Luciani et al., 2008).

The isotopic composition ($\delta^{13}C$) of DOC was determined at the UC Davis Stable Isotope Facility, following the described procedure (http://stableisotopefacility.ucdavis.edu/doc.html). Briefly, a TOC Analyzer (OI Analytical, College Station, TX) is interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) utilizing a GD-100 Gas Trap Interface (Graden Instruments).

4. Statistical analysis

Statistical analysis was performed using R (R Core Team, 2019) and the R studio software (Version 1.2.1335), using ggplot (Wickham, 2016), dplyr (Wickham et al., 2019), and dunn.test (Dinno, 2017) packages. Significant differences ($p<0.05$) between groups were evaluated using Kruskall Wallis and Dunn's post hoc multiple test.

5. Results

5.1. Trends in water chemistry from the source of the black river to the ocean

The observed water chemistry of the Ambawang river and drainage canals is typical of black rivers draining peatlands (Table 1, Figure 2), and does not show significant differences between the two sampling seasons. It is acidic with a pH of 3.2 ± 0.6 and 3.5 ± 0.3 in the drainage canals (DC) and black river (BR) respectively, has a low conductivity (DC: 89.8 ± 21.4 µS cm^{-1}, BR: 85.2±21.6 µS cm^{-1}), is hypoxic (DC: 2.3 ± 0.3, BR: 1.9 ± 0.7mg

L^{-1}), and has low nutrient concentrations (DIN < 0.3 mg L^{-1} and P-PO_4 < 0.015 mg L^{-1}) but high DOC concentrations (DC: 35.2 ± 5.9, BR: 35.8 ± 3.5 mg L^{-1}). The Cl^- concentrations are low and homogeneous (DC: 2.6 ± 0.7, BR: 2.4 ± 0.6 mg L^{-1}). After the confluence with the white river, the chemistry of the river radically changes. An abrupt increase in pH is observed (WR: 5.3 ± 0.7). The dissolved oxygen concentration increases to 3.7±1.0 mg L^{-1}, while DOC concentrations drop sharply to 9.2 ± 3.2 mg L^{-1}. We also observe a slight increase in NO_3^- and decrease in PO_4^{2-}. Across all samples, the DOC concentrations show a significant negative correlation with DO concentrations (r^2=0.63, n=40, $p<4.10^9$). In contrast, no increase in Cl^- concentration is observed until close to the ocean (3 samples corresponding to ocean water intrusion were excluded from Figure 2).

5.2. DOM optical characteristics and stable isotopic signature

No systematic differences are observed for the DOM characteristics between the two sampling campaigns. The $\delta^{13}C$ signature of DOC (Figure 3a) is very negative, reaching -30.3±0.4‰ in the drainage canals. It gradually and continually increases along the continuum from upstream in the black river to the ocean (Figure 3a). As a result, the $\delta^{13}C$ of DOC in the drainage canals and the black river, is significantly more depleted than the white river. The $\delta^{13}C$ signature of DOC is significantly negatively correlated with DOC concentration (r^2=0.68, $p<10^{-4}$, n=40), with the highest DOC values being associated with the lowest $\delta^{13}C$-DOC values.

The SUVA index (Figure 3b) has high values in the black river (5.3±1.2), with the highest values measured upstream. A wide range of values is measured in the drainage canals (4.3 ±1.4). The SUVA values of the black river are significantly higher than those measured in the Kapuas Kecil (4.5±0.3) and its tributaries (4.2 ±0.2). The fluorescence index has relatively high values for tropical peatlands, where most DOM mostly originates is of terrestrial origin (Gandois et al., 2014; Zhou et al., 2019). The values varies widely in the drainage canals (1.60±0.17) and black river (1.55±0.06), but is more uniform in the white river, both upstream (1.55±0.03) and downstream (1.55±0.05) of the confluence with the black river. Despite the high FI values, these two optical indices show coherent spatial patterns within the black river and drainage canals (Figure 3b&d). For example, lower SUVA values are associated with higher FI values, in three drainage canals and in the black river close to their connection, sampled during the second sampling campaign. Across all samples, a significant correlation is observed between FI and SUVA values (r^2=0.37, $p<10^{-4}$, n=41).

The EEMS of all water samples have two main peaks (Figure SI.2). The primary peak (λex=250 nm, λem= 460 nm), is coupled with a less intense peak (λex=350 nm, λem= 460 nm). The peaks are typical of high molecular and aromatic molecules, which have been observed in wetlands (Fellman et al., 2009). The PARAFAC analysis reveals two fluorophores: C1 (λex=255 nm, λem= 450 nm) and C2 (λex=285 nm, λem= 485 nm, Figure SI. 3) The first component constitutes from 60 to 73 % of the total fluorescence of samples. The relative contribution of these two fluorophores evolves along the sampled continuum, with the lowest values measured upstream in the black river (Figure 3c). The spatial evolution of the C1/C2 ratios and the $\delta^{13}C$-DOC values show consistent trends. A significant (r^2=0.43, p< 0.001, n=41) relationship is observed across all the samples between these two indicators. A stronger relationship (r^2=0.85, p< 0.001, n=5) is observed when the drainage canals samples alone are considered.

5.3. Trace element concentrations and physical fractionation

Black rivers originating from drained peatlands have a unique composition of inorganic elements. The concentrations of trace metals (Pb, Ni, Zn, Cd) as well as Al and Fe and are significantly higher in the black river and drainage canals than the concentrations in the white river (Table 2, Figure 4). For Al, Fe and As, high concentrations are measured in the black river during the first sampling campaign (drier conditions). In contrast to other TM, higher Cu concentrations are measured in the white river. A PCA analysis (Figure 5) of TM concentration and DOM properties reveals specific associations between DOC, Fe and As and to a lesser extend Zn and Cd, while another group is formed by Al, Pb and Ni. Cu shows no association with DOM but does show increased concentrations with higher FI. The first axis of PCA (load of DOC, Fe, As) strongly discriminates the black river and drainage canals samples from the white river.

The distributions of DOC and TM are presented in Table 3. Dissolved organic carbon is mostly (>98%) dissolved or in the form of fine colloids (<0.22 µm) along the entirety of the studied continuum. Iron and As are mostly present in dissolved form or as fine colloids in the black river and drainage canals (>96%). However, after transfer to the white river, half of Fe and a third of As is present in the coarse colloidal form. Zinc and Cd do not show similar patterns. Aluminium is mostly present in the coarse colloidal phase (>60%) in the black river and drainage canals and this proportion further increases in the white river (>80%). Lead is mostly present in the dissolved and fine colloid phase (>75%) in the drainage canals and black river and shifts to coarse colloidal (>60%) forms after the confluence with the white river. Nickel and Cu are mostly present in the dissolved and fine colloidal phase in the DC and BR but almost entirely in the coarse colloidal fraction in the white river.

5.4. Pb isotopic composition

We observe distinct differences between the lead isotope ratios in the white river and those in the black river and drainage canals. A decrease in the $^{206}Pb/^{207}Pb$ isotopic ratio is observed with increasing Pb concentrations in the black river but not the white river (Figure 6a). Futhermore, the biplot of the $^{206}Pb/^{207}Pb$ and the $^{208}Pb/^{206}Pb$ signatures illustrate significant differences between the white water and black river/drainage canal groups (Figure 6b).

6. Discussion

6.1. In-stream processing of DOM in black rivers

We observe in-stream processing of DOM, but the total DOM exported from tropical peatlands exceeds the processing capacity of the rivers which drain them and a large proportion of DOM is transported to the ocean. We find persistently high DOC concentrations in both drainage canals and black rivers draining degraded peatlands consistent with the range of previously reported values in Borneo (Cook et al., 2018; Moore et al., 2011) and in the upper range of black rivers in Sumatra (Rixen et al., 2008; Baum et al., 2007) . We also find indicators of in-stream processing of DOM. The transformation of DOM we observe along the continuum is likely primarily due to photo-oxidation with a smaller contribution from microbial processing. We observe an increase in the $\delta^{13}C$-DOC values along the studied continuum (Figure 3a). This shift toward higher $\delta^{13}C$-DOC is correlated with an

increase in the C1/C2 ratio of PARAFAC fluorophores (Figure 3c). The two fluorophores are typical of terrestrial input of DOM (Yamashita et al., 2008), and similar to observed fluorophores in other black rivers in Borneo (Harun et al., 2015; Zhou et al., 2019). An increase in this C1/C2 ratio reflects a shift toward lower wavelengths and therefore toward lower aromaticity and lower molecular weight (Austnes et al., 2010; Zhou et al., 2019). Moreover, a decreasing trend in SUVA values is observed along the continuum (Figure 3b). These observations indicate that at our site, aromatic features are preferentially processed in-stream, consistent with a dominant effect of photo-oxidation (Amon and Benner, 1996; Sharpless et al., 2014; Spencer et al., 2009). This has also been observed in the Congo River where photo-oxidation led to an increase in δ^{13}C-DOC and a decrease in aromatic features (Spencer et al., 2009).

However, photo-oxidation is not the only process responsible for the processing of DOM. The low oxygen levels in the black river and drainage canals and the significant relationship between DOC and DO concentrations suggest that nearly all oxygen entering the well-mixed water is quickly consumed by DOM oxidation (Figure 2a&b). Furthermore, the sharply decreasing oxygen profiles measured in the black river suggest that the transformation of DOM is restricted to the shallow surface layers of these waters (Figure SI.3). Additionally, localized increases in fluorescence index, coupled with decreases in SUVA (reflecting a higher proportion of microbial derived DOM, Figure 3d) suggest that microbial processing occurs in some locations in drainage canals. Both photo-oxidation and microbial processing have been quantified in laboratory experiments for DOM originating from tropical peatlands. Martin et al. (2018) found that up to 25 % of riverine DOC from a black river in Sarawak, Malaysia, was lost within 5 days of exposure to natural sunlight. Microbial long-term incubation studies by (Rixen et al., 2008), showed that 27% of DOC was degraded after two weeks. In black rivers, it is likely that in-stream microbial processing of DOM is limited by the low oxygen concentrations, low pH, and low nutrient levels (especially inorganic nitrogen), (Wickland et al., 2012), rather than intrinsic refractory characteristics. Although the precise extent of in-stream processing cannot be quantified here, our results are consistent with in stream transformation of DOM by photo-oxidation as well as some contribution of microbial degradation in the shallow surface layers. In the future, quantitative assessment of outgassing in tropical peatland drainage canals would improve the evaluation of carbon release following peatland drainage. Overall, more work is needed to understand the extent of upstream processing of peatland DOM.

6.2. Role of DOM, Al and Fe in trace metal dynamics in peat draining waters

This study provides the first record of trace metals in black rivers originating from degraded tropical peatlands. We observe strong enrichment of Al and Fe, as well as Pb, As, Ni and Cd in peat-draining waters. The measured concentrations are comparable to those measured by Kurasaki et al. (2000) in Borneo rivers for Pb, Zn, Cu and Cd, but significantly higher (5 to 10 times) for Fe. The concentration levels, however, remain low compared to highly impacted regions of Indonesia (Arifin et al., 2012). The elevated concentrations of Al and Fe in water draining tropical peatlands is consistent with existing observations of elevated Fe concentrations from black rivers in the tropics (Zhang et al., 2019) and northern peatlands. This enrichment is likely due to the weathering of mineral material under the peat during peat accumulation processes (Tipping et al., 2002; Pokrovsky et al., 2005). As a consequence, in water draining peatlands, strong organo-mineral associations between DOM and Fe (Krachler et al. 2010, 2012; Broder and Biester 2015), as well as DOM and Al (Helmer et al., 1990) have been observed. These

colloidal associations between DOM and Al and Fe in the form of hydroxides strongly control TM transfer and speciation in peat draining waters (Tipping et al., 2002). In the present study, specific associations of trace metals with Al and Fe are observed, including strong links between Al and Pb and Ni. However, the lack of a direct relationship between Pb and DOM contrasts with reported observations in the literature (Graham et al., 2006; Jeremiason et al., 2018; Pokrovsky et al., 2016). Despite this, we do observe strong links between Fe, As, Zn, Cd and DOM, which have been previously reported in water draining peatlands (Broder and Biester, 2015; Neubauer et al., 2013; Pokrovsky et al., 2016). The coupled dynamics of Fe and As might be related to similar mobilization processes within the peat column, with the sorption of As to Fe(III)-(oxyhydr)oxides (ThomasArrigo et al., 2014) in anoxic peat water. Widespread drainage of tropical peatlands and the corresponding release of anoxic water to surface water networks could induce a coupled increase in DOM and Fe concentrations, similar to that which has occurred in Sweden (Kritzberg and Ekström, 2011).

6.3. Peatlands as secondary sources of atmospheric pollutants

The isotopic composition of Pb in peat draining water strongly suggests it is of anthropogenic origin. The isotopic signatures measured in river samples are a combination of the signature of undisturbed soils of Borneo (Valentine et al., 2008), and a mix of both present and past anthropogenic inputs. Older anthropogenic inputs are reflected by the signature of atmospheric deposition from Java aerosols (Bollhöfer and Rosman, 2000), while the signature of recent regional anthropogenic inputs was characterized by rain samples collected in Pontianak as part of this study (Figure 6b). In the black river and drainage canals, the isotopic ratio is close to that of aerosols and recently sampled rainwater and is dominated by anthropogenic inputs, whereas the isotopic ratio in the white river is closer to the natural signal (Figure 6). This isotopic difference is consistent with the difference between the watersheds drained by these two rivers: tropical peatlands are ombrotrophic systems, and the trace metal content in peat soil is derived from the atmosphere (Weiss et al., 2002), whereas the Kapus Kecil is recharged from a larger watershed and reflects contribution of mineral soils. Tropical peatlands can serve as secondary sources of atmospheric pollutants to the environment. With peatland drainage, black rivers release the accumulated atmospheric deposition over hundreds of years on much shorter timescales. For example, the isotopic signature observed in the black river reflects anthropogenic sources deposited at different times, including older deposition such as the lead measured in the Java aerosols (Bollhöfer and Rosman, 2000), and more recent deposition following the widespread introduction of unleaded fuel (characterized by samples collected from rainwater during the January 2014 sampling period in this study). This release of lead by degraded tropical peatlands has the potential to impact records from environmental archives, for example the corals of the Singapore Strait (Chen et al., 2015). Although this is the first measurement of the aquatic release of trace metals from tropical peatlands, the role of tropical peatlands as a secondary source of contaminants has also been highlighted by the trace metal content analysis of dust emitted to the atmosphere by peat fires (Betha et al., 2013).

6.4. From degraded tropical peatlands to the ocean

Sharp changes in physico-chemical conditions are observed after the mixing of the black and the white river, including sharp increases in DO concentrations and pH values. This strongly controls the transport of DOM and TM drained from degraded tropical peatlands. After the confluence with the white river, DOC concentrations decrease abruptly. This decrease primarily results from the dilution of the black river signal. However, the sudden

elevation of pH and DO after the confluence might create favorable conditions for microbial processing of DOC, making the mixing zone a likely hotspot of GHG emissions (Palmer et al., 2016).. This would also be consistent with the decrease in the SUVA index observed after the confluence. Despite processing of DOM along the continuum, a significant proportion of DOM originating from degraded peatlands actually reaches ocean. We observe high DOC concentrations at all sampling locations, with concentrations remaining high even close to the ocean (Figure 2a). Additionally, the results of our physical fractionation show that even close to the estuary, DOC remains in the dissolved and fine colloid form (<0.22 µm), and that flocculation processes might be limited. Then, the important proportion of coastal peatlands in Indonesia and Malaysia results in the relatively high fluvial organic carbon export reported in to South China Sea (Huang et al., 2017).The decrease in trace metal concentrations after the confluence might be influenced by shifts in physical fractionation and an increased proportion of colloidal form. This is especially true for Al and Pb. Some flocculation at the estuary might limit their transfer to the ocean. For Fe and As, a higher proportion remains in the form of fine colloids after mixing with the whiter river, and is still associated with DOC. Similar conservative behavior of LMW organic molecules associated with Fe was observed at the outlet of northern peatlands (Krachler et al., 2012), and in Arctic rivers (Pokrovsky et al., 2014). This highlights that dissolved organic molecules derived from tropical peatlands can also act as carriers of trace metals to the ocean.

7. Conclusions

This study characterizes the composition and concentration of DOM and TM in the canals and rivers draining the degraded tropical peatlands of Indonesian Borneo. It highlights in-stream processing of DOM in drainage canals and rivers draining degraded peatlands. Both stable isotopic and optical properties of DOM are consistent with photo-oxidation along the continuum from the black river to the ocean. In the black river and drainage canals, rates of microbial processing are likely limited by the low dissolved oxygen concentrations, and limited to shallow depths. Along the continuum, DOM is found at relatively high concentrations in the dissolved and fine colloidal phases, suggesting a substantial fraction of DOM derived from degraded peatlands reaches the ocean. Additionally, we provide the first assessment of trace metal concentrations in rivers draining degraded tropical peatlands. Rivers draining these peatlands are enriched in some trace metals (Pb, Ni, Zn, Cd) as well as Al and Fe. Using the isotopic signature of Pb, we show that degraded tropical peatlands are secondary sources of atmospherically deposited contaminants to surface waters. Trace metal dynamics after transfer to the white river show clear trends: while Pb and Ni are associated with Al; As, Zn and Cd are associated with Fe and DOM. Lead and Al are present in coarse colloidal form and may be transferred to sediments after flocculation. In contrast, DOM, Fe and As are found predominantly in fine colloidal form even after the confluence with the white river, and as a result may be transferred to the ocean. The role of degraded tropical peatlands as a source of DOM, as well as Fe and As to the ocean requires further investigation.

Author contribution

LG, AMH, GH and CFH designed the study. LG, AMH, MN and GH conducted field campaigns. SM and LG conducted fluorescence analysis. GLR and AC conducted lead isotope analysis. LG and AMH wrote the manuscript, with inputs from all co-authors.

Competing interests

The authors declare no competing interests.

Data availability

The data are available at https://doi.org/10.5194/bg-2019-253.

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Table 1. Mean and standard deviation (mean±sd) of pH, conductivity and main elemental concentrations of the white river, and upstream of the white river, black river and drainage canals for the two sampling campaigns (June: drier period, January, wetter period). DO: Dissolved oxygen, FI: Fluorescence Index, SUVA: Specific UV Absorbance).

		n	pH /	DO mg L^{-1}	Cond µS cm^{-1}	SM mg L^{-1}	DOC mg L^{-1}	N-NO_3 µmol L^{-1}	N-NH_4 µmol L^{-1}	P-PO_4 µmol L^{-1}	Cl^- mg.L^{-1}	δ^{13}DOC ‰	FI -	SUVA L.mg^{-1}.m^{-1}
White River	dry	5	5.2 ± 0.33	4.49 ± 0.26	37.2 ± 13.2	47.9 ± 13.2	8.43 ± 1.61	0.192 ± 0.062	<DL	<DL	4.83 ± 4.03	-29.46 ± 0.23	1.63 ± 0.08	3.4 ± 0
	wet	5	4.43 ± 0.86	3.37 ± 0.96	1220.6 ± 981.8	21.1 ± 2.5	11.25 ± 4.29	0.043 ± 0.049	<DL	0.003 ± 0.249	409 ± 342	-29.41 ± 0.41	1.64 ± 0.04	4.6 ± 0.3
White River upstream	dry	2	5.45 ± 5.71	4.91 ± 0.17	24 ± 3.8	55.7 ± 17.2	6.89 ± 1.28	0.196 ± 0.033	<DL	<DL	1.31 ± 0.64	-29.32 ± 0.06	1.54 ± 0	n.a
	wet	3	5.37 ± 0.06	4.15 ± 0.39	268.7 ± 92	29.4 ± 10.1	8.69 ± 0.78	0.061 ± 0.011	<DL	0.005 ± 0.404	47.9 ± 65.2	-29.56 ± 0.13	1.57 ± 0.01	4.1 ± 0.1
Black river	dry	8	3.45 ± 0.06	1.69 ± 0.39	98.7 ± 18.2	23.7 ± 19.1	36.42 ± 2.54	0.092 ± 0.042	0.120 ± 0.091	0.023 ± 2.32	2.78 ± 0.5	-30.29 ± 0.38	1.7 ± 0.04	4.8 ± 0.4
	wet	11	2.97 ± 0.13	1.98 ± 0.75	77.3 ± 18.3	13.4 ± 8.5	35.37 ± 3.7	0.043 ± 0.022	0.014 ± 0.028	0.014 ± 1.22	2.2 ± 0.6	-30.04 ± 0.38	1.8 ± 0.09	4.9 ± 1.3
Drainage canal	wet	6	3.08 ± 0.43	2.34 ± 0.3	89.8 ± 19.6	n.a	35.17 ± 5.47	0.034 ± 0.033	0.020 ± 0.039	0.021± 1.65	2.6 ± 0.6	-30.27 ± 0.4	1.8 ± 0.13	4.3 ± 1.3

Table 2. Mean and standard deviation (mean±sd) of trace meatal concentration of the white river, white river tributaries, black river and drainage canals for the two sampling campaigns (June: drier period, January, wetter period).

		n	Al µg.L^{-1}	Fe µg.L^{-1}	Ni µg.L^{-1}	Cu µg.L^{-1}	Zn µg.L^{-1}	Pb µg.L^{-1}
White River	dry	5	312 ± 407.1	444.9 ± 383.9	0.53 ± 0.11	1.14 ± 0.16	18.57 ± 9.028	0.262 ± 0.236
	we t	5	147.2 ± 124.6	547.5 ± 497.3	1.19 ± 1.17	0.87 ± 0.09	10.26 ± 6.14	0.129 ± 0.102
White River upstream	dry	2	101.61 ± 27.5	242.5 ± 44.5	0.52 ± 0.08	1.06 ± 0.01	15.29 ± 3.06	0.139 ± 0.027
	we t	3	148.6 ± 72	408.7 ± 170.2	0.72 ± 0.44	1.19 ± 0.24	9.7 ± 6.23	0.236 ± 0.167
Black river	dry	8	592.8 ± 43	2143.5 ± 187.6	1.96 ± 1.67	0.58 ± 0.19	119.38 ± 86.47	0.467 ± 0.054
	we t	1	443.1 ± 137.5	1441 ± 493.5	1.3 ± 0.53	0.72 ± 1.13	10.95 ± 6.98	0.316 ± 0.11
Drainage canal	we t	6	489.2 ± 194.9	1348 ± 494.1	1.54 ± 0.8	0.37 ± 0.07	14.52 ± 11.62	0.313 ± 0.048

601 **Table 3.** Proportion of DOC and selected trace metals in the form of dissolved and fine colloids (< 0.22 µm) and
602 coarse colloids (0.2-2.7 µm)

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	Drainage Canals		Black River		White River	
	<0.2 µm	0.2-2.7 µm	<0.2 µm	0.2-2.7 µm	<0.2 µm	0.2-2.7 µm
DOC	97	3	98	2	100	0
Al	39	61	36	64	18	82
Fe	100	0	99	1	45	55
Pb	75	25	78	22	34	66
As	98	2	96	4	67	33
Ni	72	28	50	50	1	99
Cu	68	32	48	52	1	99
Zn	13	87	12	88	26	74
Cd	66	34	100	0	83	17

604

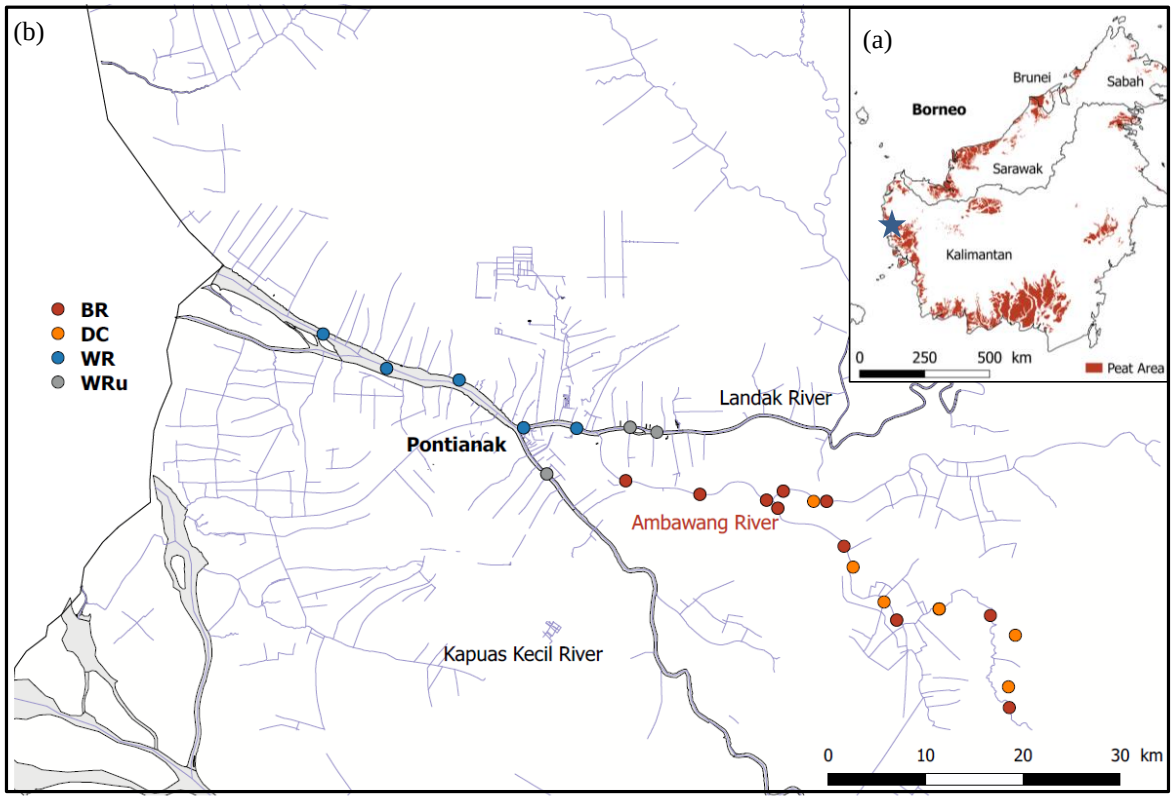

Figure 1: (a) Location of the study area on Borneo island. (b) Location of sampling sites and types of water: Black River (BR). Drainage Canals (DC). White River (WR). and white River upstream of the confluence with the black river (WRu).

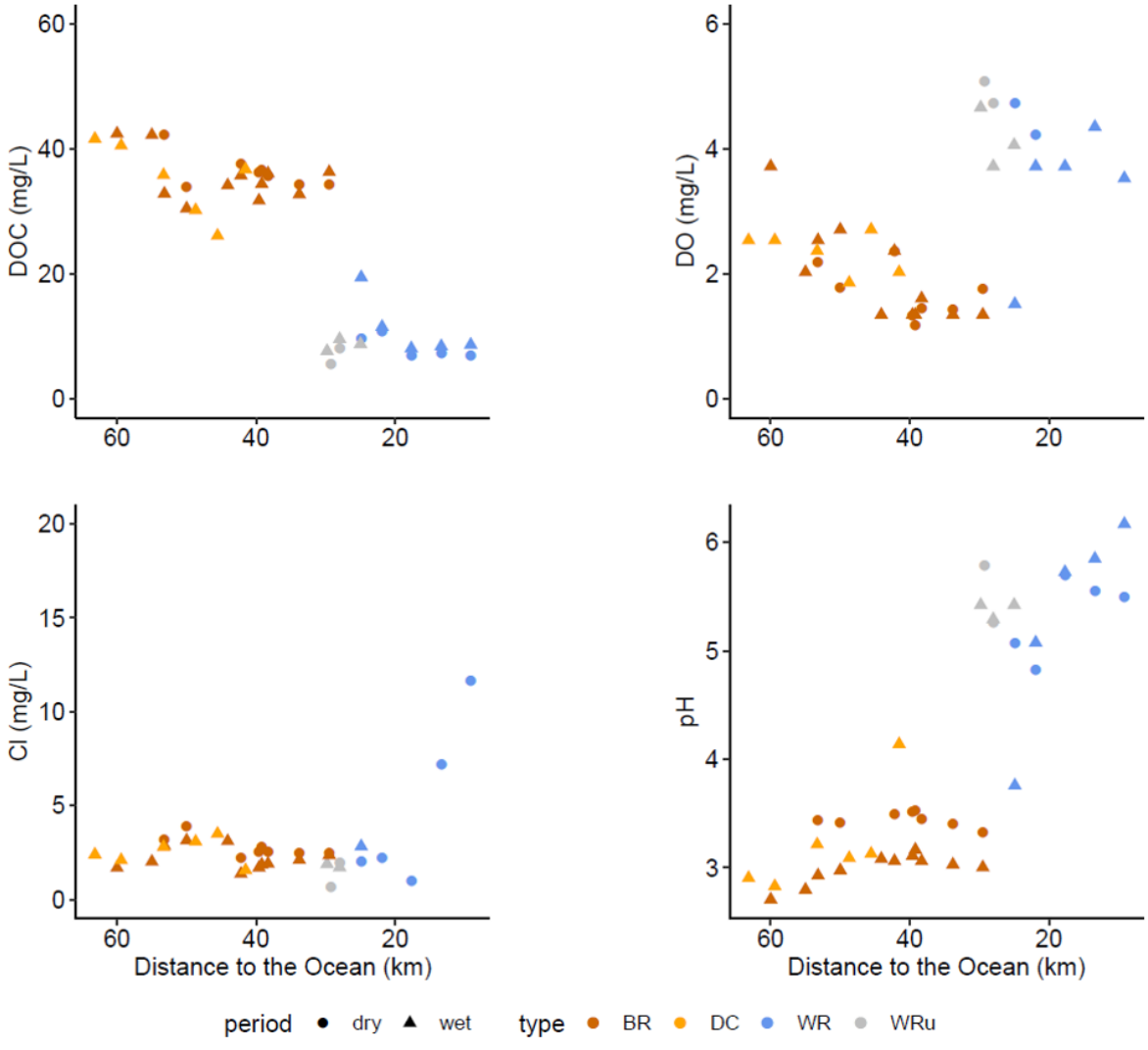

Figure 2: Evolution of (a) dissolved organic carbon concentration. (b) dissolved oxygen concentration. (c) chloride concentration and (d) pH along the continuum from the black river to the ocean.

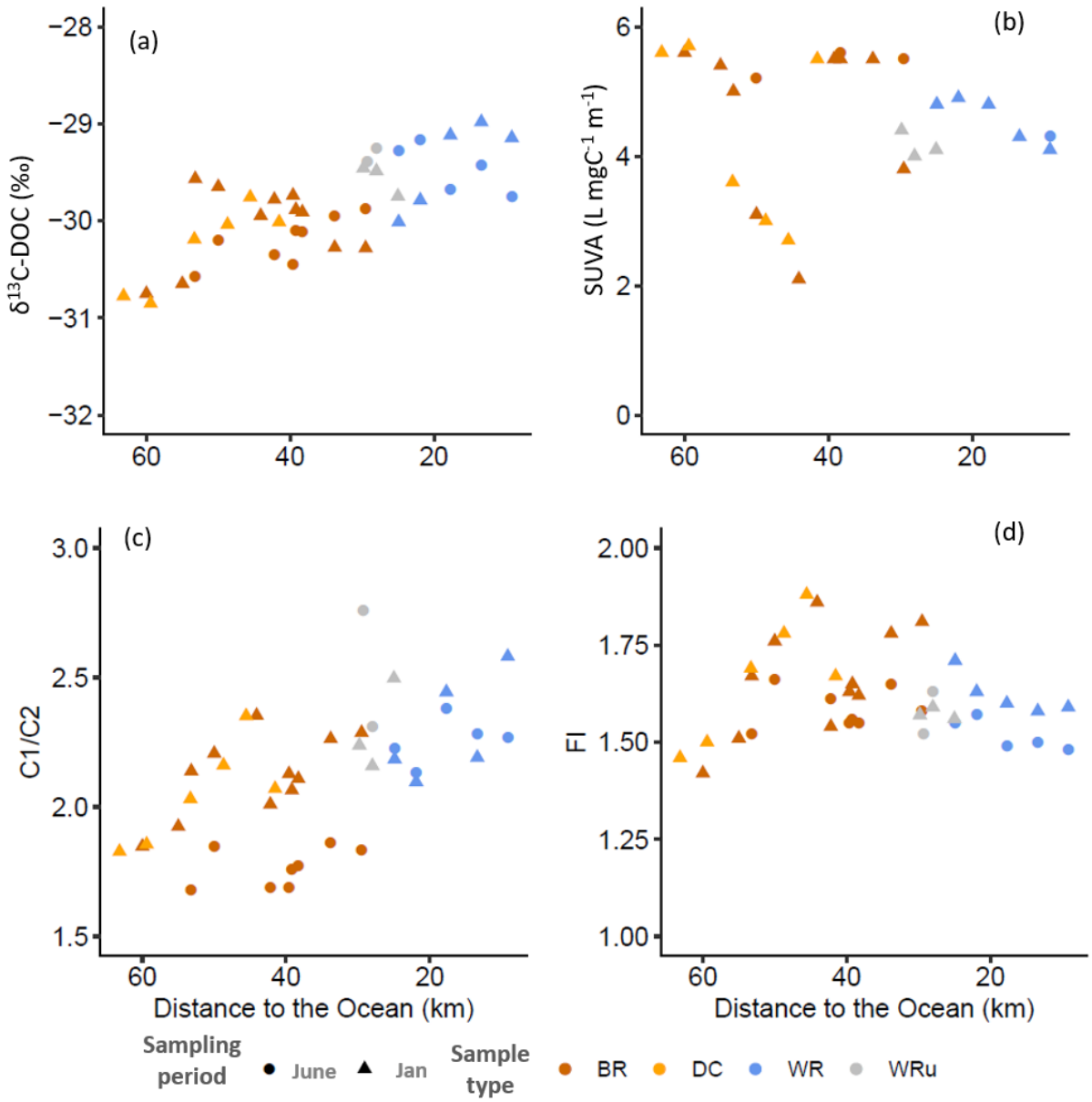

Figure 3: Evolution of DOM along the black river to the ocean continuum. (a) δ^{13}C-DOC. (b) SUVA (Specific UV Absorbance) index. (c) C1/C2. (d) FI (Fluorescence Index).

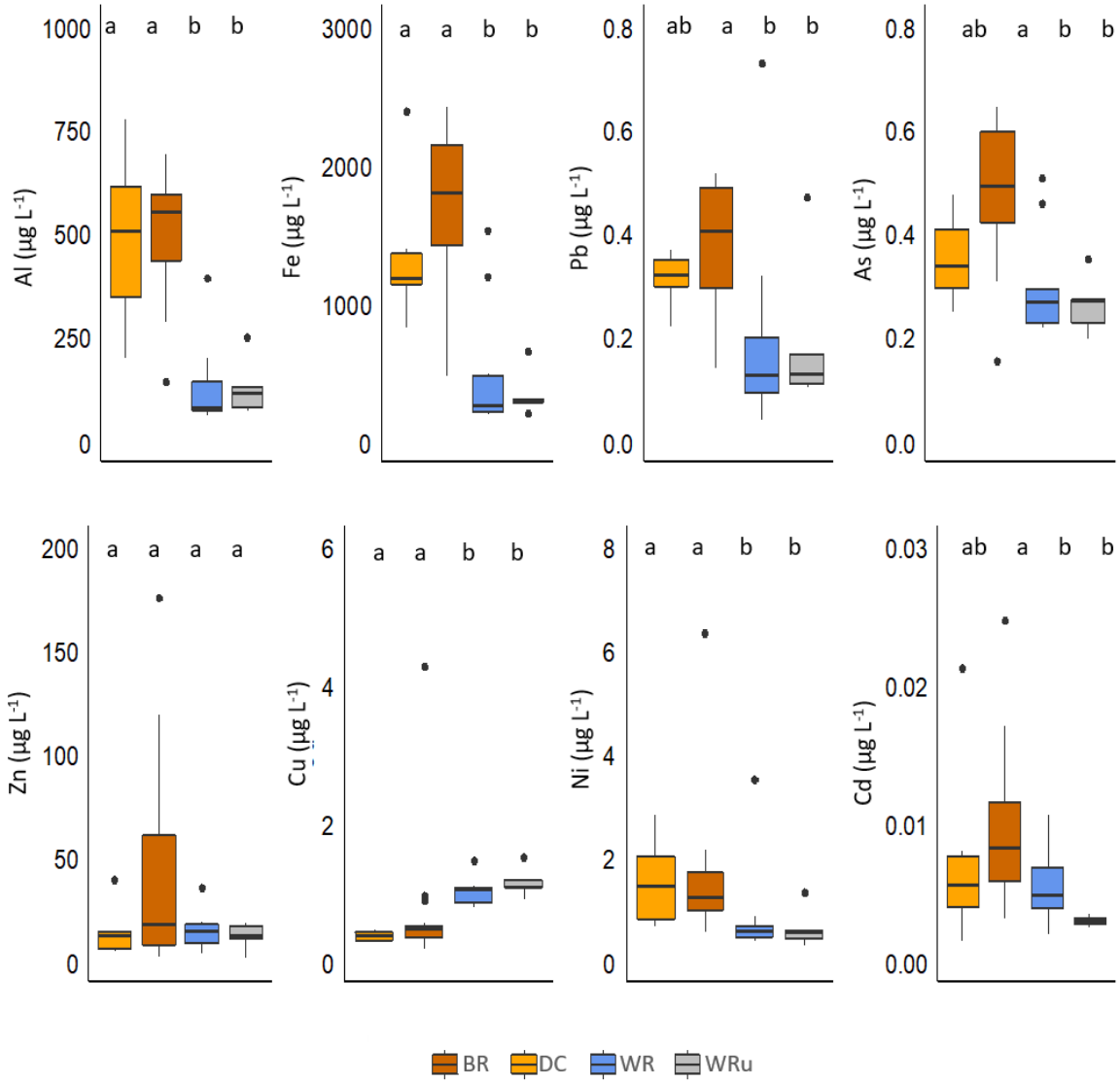

Figure 4: Ranges of selected TM concentration for different sampled water types. Letters represent significantly different groups (Kruskall Wallis and Dunn's post hoc multiple test ($p<0.05$)). The black line is the median. The lower and upper levels of the box represent the 25 and 75 % quartile. respectively. The lower whisker is smallest observation greater than or equal to lower hinge - 1.5 * IQR (inter-quartile range). the upper whisker. the upper whisker is the largest observation less than or equal to upper hinge + 1.5 * IQR.

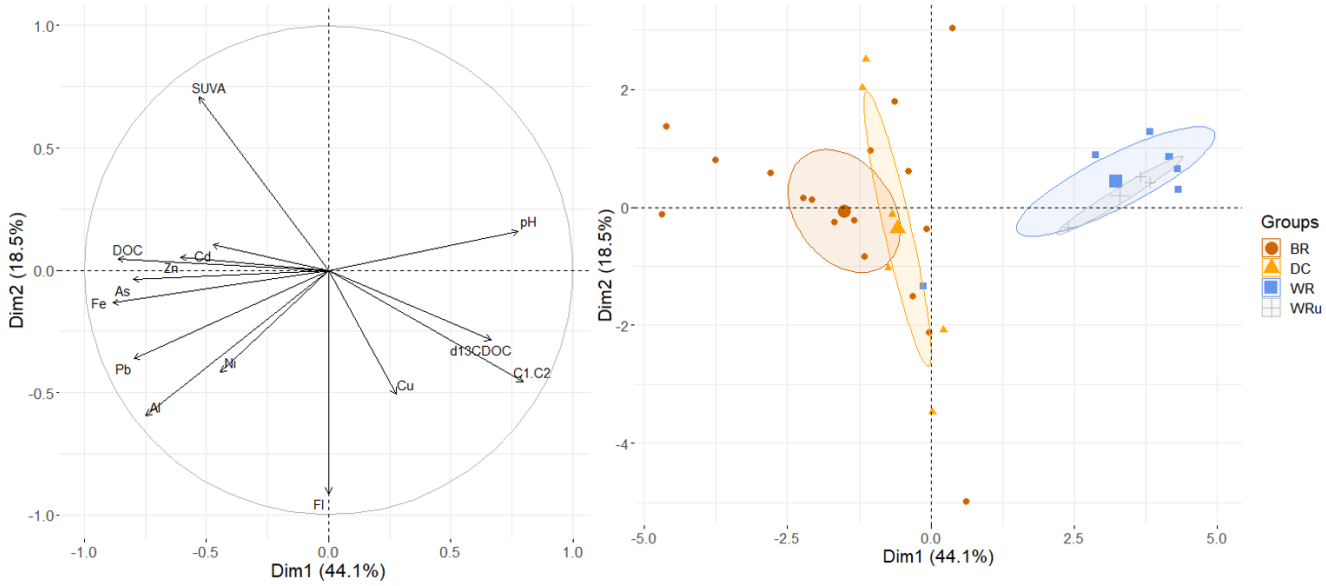

Figure 5: The first two factors of the PCA (63.1 % of variance) by variables (a) and by observation (b) for the different sampled water types.

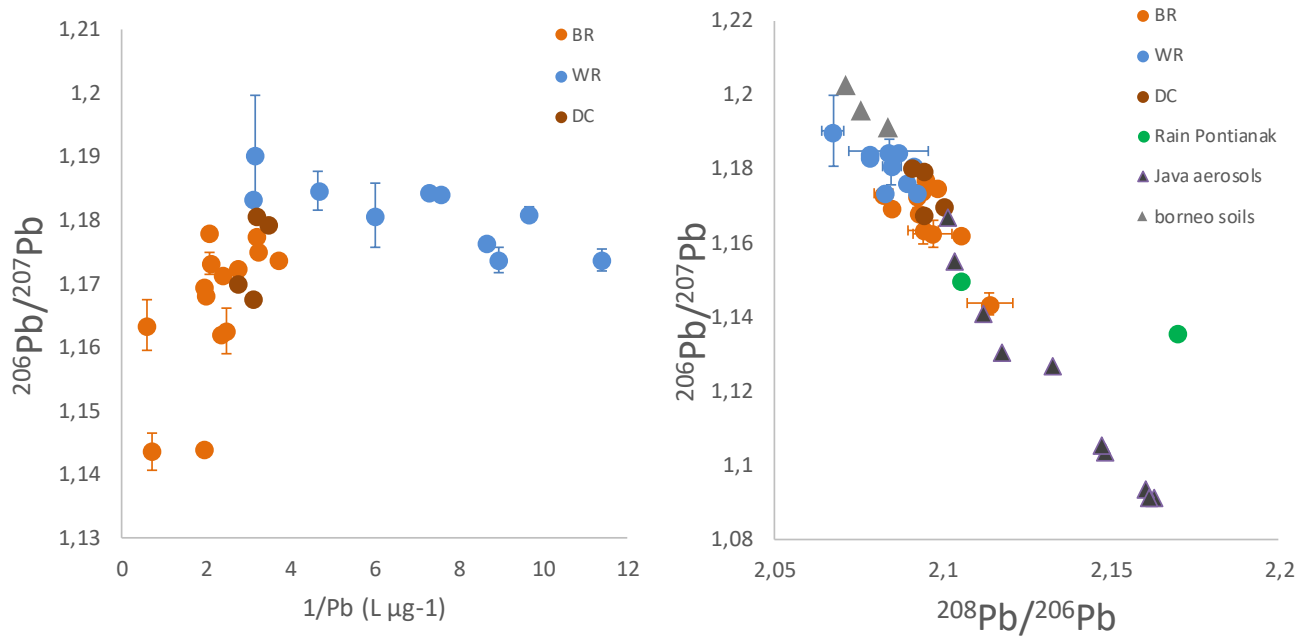

Figure 6: (a) Dependence of $^{206/207}$Pb ratio on Pb concentrations for the different water samples. (b) Relationship between ^{206}Pb/^{207}Pb ratio and ^{208}Pb/^{206}Pb ratio. The error bars represent the +/- standard deviation.

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