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Key Points:

- The Congo River is an important source of trace metals (TMs) to the South Atlantic Ocean revealed by data from GEOTRACES cruise GA08
- Wet deposition (rainfall) is identified as an additional TM source to the Congo plume by concurrently considering river and rain data
- Rainfall supplies anthropogenic dTMs (Cd, Cu, Pb and Zn) with fluxes equivalent to 20%–68% of those from the Congo River on the Congo shelf

Supporting Information:

Supporting Information may be found in the online version of this article.

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Trace Metal Fluxes of Cd, Cu, Pb and Zn From the Congo River Into the South Atlantic Ocean Are Supplemented by Atmospheric Inputs

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Abstract The Congo River supplies vast quantities of trace metals (TMs) to the South Atlantic Ocean, but TM budgets for the Congo plume derived using radium isotopes for GEOTRACES cruise GA08 suggest additional input other than the river outflow. Considering the tight correlations between most dissolved TMs and salinity in the plume and the high rainfall during the wet season over the Congo shelf, we hypothesized that wet atmospheric deposition is a TM source to the Congo plume. Observed TM concentrations in rainwaters across the Congo shelf were mostly comparable to values from previous work in the North Atlantic and Mediterranean Sea. Wet deposition contributed the equivalent of 43% dCd, 21% dCu, 20% dPb and 68% dZn of the Congo River fluxes. Our findings show an important role of wet deposition in supplying TMs to the South Atlantic overlapping with the region that receives substantial TM fluxes from the Congo River.

Plain Language Summary The Congo River has the second largest freshwater discharge volume globally and creates an extensive near-equatorial plume into the Atlantic Ocean. The Congo plume constitutes an important source of trace metals (TMs) to the ocean, which impacts biogeochemical cycles in the tropical and subtropical ocean. However, existing work suggests a discrepancy within the TM budgets in the Congo plume and points to unknown source other than the Congo River or shelf sediments. Most TM concentrations across the Congo plume remain tightly correlated with salinity, suggesting that any additional sources are likely also freshwater-derived or enter the ocean at the river mouth coincidently with direct riverine TM inputs. Here, TM concentrations in ocean, river and rainwater collected during the GEOTRACES GA08 cruise are combined to suggest that wet deposition augmented some Congo TM fluxes to the ocean. Fluxes of anthropogenic Cd, Cu, Pb and Zn to the Congo shelf from wet deposition are of the same order of magnitude as the Congo River. Concentrations of these elements in rainwater are similar to prior observations reported for the North Atlantic and Mediterranean Sea, suggesting that a large fraction of the global range of rainwater concentrations over the ocean has been captured in our observations.

1. Introduction

Trace metals (TMs) are supplied to the surface ocean by shelf sediments (Elrod et al., 2004; Liu et al., 2022b), rivers (Buck et al., 2007) and atmospheric deposition (Jickells, 1995), affecting primary productivity and hence ocean carbon uptake and other ecosystem services (Moore et al., 2013; Twining & Baines, 2013). The Congo River discharges ~41,000 m^3 s^{-1} of freshwater, and creates a freshwater plume extending over 800 km offshore, with its flow directed by a slow equatorward current and dispersal of the plume limited by low Coriolis forces in the near-equatorial southeast Atlantic Ocean (Braga et al., 2004; Laraque et al., 2009). The plume constitutes a major source of TMs to the ocean including iron (Fe), manganese (Mn) and cobalt (Co) (Vieira et al., 2020), and influences ecosystem functioning in the South Atlantic (Browning et al., 2017). Such an extensive off-shelf plume of TMs associated with a river outflow and reaching an ocean gyre is unusual in the global ocean. This is particularly the case for dissolved Fe (dFe), because estuarine processes typically remove ~90%–99% riverine dFe in low salinity waters (Boyle et al., 1977). Whilst other dTMs such as dMn behave generally more conservatively during estuarine mixing (Moore et al., 1979; Wilke & Dayal, 1982), it is still unusual that river plumes enriched in dTMs are found so far off shelf (GEOTRACES Intermediate Data Product Group, 2021).

Questions remain concerning the mechanisms by which such high TM concentrations in the plume are maintained. Prior work using the radiogenic radium isotope ^{228}Ra and Fe isotope composition ($\delta^{56}Fe$) suggests

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that the riverine fluxes of dFe and several other TMs are augmented by additional sources (Hunt et al., 2022; Vieira et al., 2020). However, a shelf sediment source is not consistent with the observed heavy δ^{56}Fe signature (δ^{56}Fe > +0.33‰) of the plume (Hunt et al., 2022). Similarly, estimates of dry atmospheric deposition for the same cruise appear to be too low (e.g., < 1 nmol m^{-2} day^{-1} for all TMs, Barraqueta et al., 2019) and would not directly explain the close correlations between most TMs and salinity. Whilst many processes could potentially supply TMs to shelf environments, many of these are implausible as major additional features of TM budgets in the Congo shelf region because they are inconsistent with the observed relatively tight correlations between dTM concentrations and salinity, and/or the enrichment of dTMs in surface waters only.

We hypothesize that wet deposition could be a potential TM source. The Congo shelf is characterized by high precipitation rates of >200 mm per month during the period between October and December (Alsdorf et al., 2016; Bultot, 2019), coincident with the timing of GEOTRACES cruise GA08 (Figure 1). Such precipitation is not only of great importance to the freshwater discharge of the Congo River (Chao et al., 2015), but also likely contributes enhanced TM fluxes by wet deposition (Chance et al., 2015; Schlosser et al., 2014; Shelley et al., 2017). Precipitation typically has a low pH (pH < 6) and is subject to a high photon flux, both of which increase the lability, and potentially bio-availability of a range of TMs (Kieber et al., 2001, 2003a; Lim et al., 1994; Paerl et al., 1999). Yet, evaluation of the role of wet deposition in marine TM budgets is hampered by limited historical sample collection due to the obvious logistical problems with sampling of rain events at sea (e.g., Baker et al., 2013). To the best of our knowledge, the fluxes and impacts of TMs from wet deposition in the plume of a major river have not been constrained in prior budgets by concurrently considering both rainwater and seawater samples.

In order to determine the TM fluxes from the Congo and the relative importance of atmospheric deposition (wet and dry) to the surface ocean over the spatial scale of the Congo River plume, we analyzed dTM concentrations in surface waters, full-depth profiles and rainwater collected during GEOTRACES cruise GA08 on RV Meteor (M121) (Frank et al., 2014). Additionally, freshwater samples were collected directly in the Congo River during three seasons (May, July and October in 2017). Analyzed dTMs included cadmium (Cd), Co, copper (Cu), Fe, Mn, nickel (Ni), lead (Pb) and zinc (Zn). Total dissolvable TM concentrations (TdTM) in rainwater were also analyzed. Cruise GA08 took place during the wet season, between 22 November and 27 December 2015. In this study, we define two regions of interest: the Congo shelf (<500 km to the Congo River mouth; experiencing high rainfall) and the offshore Congo plume at ~3°S (>500 km to the Congo River mouth with less rainfall) (Figure 1).

2. Materials and Methods

2.1. Sampling and Analysis

Seawater samples in depth profiles were collected using 12 L TM clean Go-Flo bottles (Ocean Test Equipment) mounted on a CTD rosette frame (TM clean, General Oceanics), and surface waters were collected with an underway towfish system. Surface seawater sampling on the Congo shelf was regular when the ship was underway, and samples were thus always collected within 3 hr of rain events (Figure S1 in Supporting Information S1). Rainwater was sampled using an acid-cleaned high density polyethylene funnel positioned on the monkey island of the vessel, mounted forward of any other equipment (Table S1 in Supporting Information S1). Congo River freshwater samples were collected using a small boat during different seasons in 2017 (Table 1). River and rainwater samples for analysis of TM concentrations, were stored following filtration (dTM) and also without filtration (TdTM). For seawater only dTMs concentrations are reported. River and seawater were filtered through 0.8/0.2 µm cartridge filters (AcroPak® 1000), whereas rainwater samples were syringe filtered through 0.20 µm filters (Millipore, polyvinyl difluoride). All samples were acidified to pH ~1.9 with ultrapure HCl (Romil).

Concentrations of TMs in sea, river and rainwater samples were analyzed via high-resolution isotope inductively coupled mass spectrometry (HR-ICP-MS, ELEMENT XR, ThermoFisher Scientific) after offline pre-concentration using a SeaFAST system (SC-4 DX SeaFAST pico, Elemental Scientific Inc.) exactly per Rapp et al. (2017). Rainwater and river water samples were additionally analyzed without preconcentration due to the broad range of plausible TM concentrations with results from both analysis in close agreement. Results were validated by certified reference materials SAFe S, SAFe D2, GSP, NASS 7 and CASS 6 (Table S2 in Supporting Information S1). Detailed descriptions regarding sampling and analysis can be referred to Text S1 in Supporting Information S1.

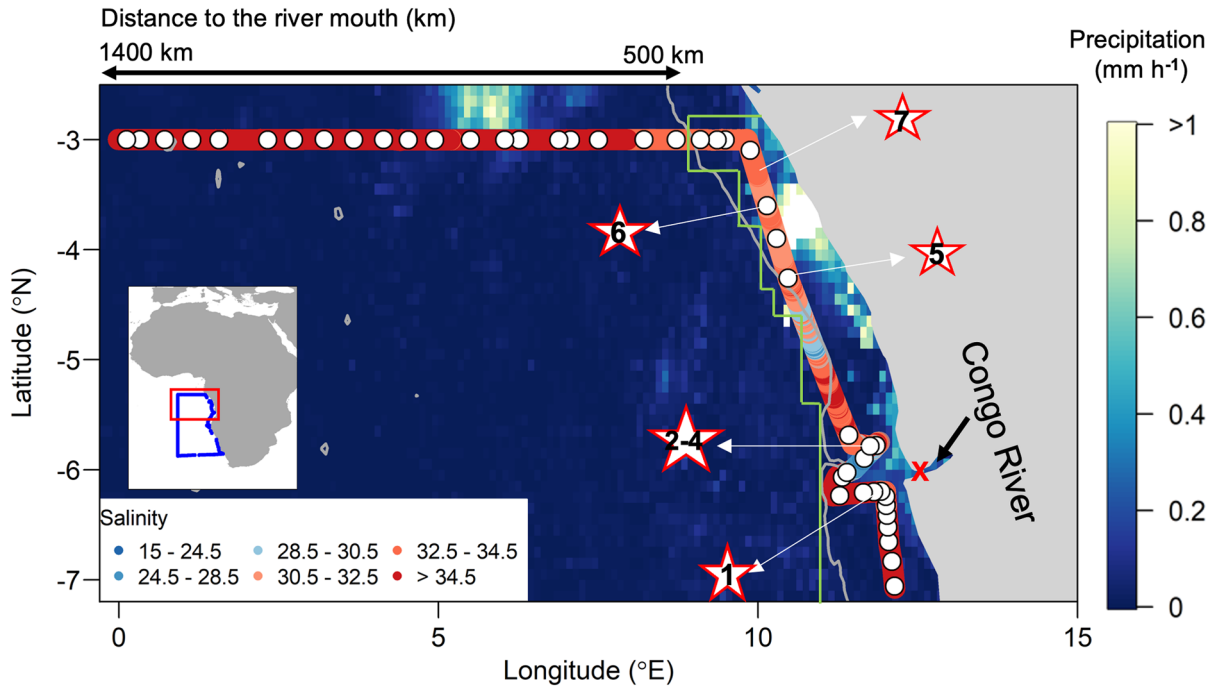

Figure 1. Overview of the study region. Cruise track showing salinity gradients (colored dots), surface water sampling locations (white circles) and rain event locations (numbered stars). The dark gray line shows the 1,500 m depth contour (NOAA ETOPO1 database) (Amante & Eakins, 2009) and the green line highlights the Congo shelf region used for calculating area-averaged precipitation rate (mm h^{-1}). Data for precipitation rates (mm h^{-1}) were download from satellite data product GPM IMERG Final Precipitation L3 Half Hourly 0.1° × 0.1° V06 (GPM_3IMERGHH) (Huffman et al., 2019) within the period of sailing within the Congo shelf region from 29 November 09:00 UTC to 02 December 05:59 UTC (color shading). Sampling location of the Congo River water (~6°S, 12.5°E) is indicated by a red cross (Rahlf et al., 2021). Salinity data were retrieved from the vessel's underway system (DSHIP Landsystem, http://dship.bsh.de/). In-set map displays a wider region and the whole GA08 transect during the remainder of which no further rain events were observed.

2.2. Data Assessment

Volume-weighted-mean TM concentrations (C_{rain}, dTM and TdTM) in rainwater were calculated for further assessments. Enrichment Factors (EFs) ($[TM/Al]_{sample}/[TM/Al]_{UCC}$) and fractional solubility of TMs ($[TM]_d/[TM]_{Td} \times 100\%$) were used to ascertain potential anthropogenic TM perturbations in the rainwater samples (Baker & Croot, 2010; Baker et al., 2013). Subscripts of sample, UCC (Rudnick & Gao, 2014), d and Td represent rainwater samples, upper continental crust, dissolved, and total dissolvable concentrations, respectively.

Additional calculations are described in detail in Text S2 in Supporting Information S1, including surface TM inventories, fluxes of TMs from rain and river, and fluxes of freshwater at the beginning of the offshore Congo plume to the ocean (Figure S2 in Supporting Information S1).

Table 1
Endmember dTM Concentrations (Mean ± Standard Deviation, nM)

	Collection date/ cruise	Salinity	Cd	Co	Cu	Mn	Fe	Ni	Pb	Zn
			(nM)							
Congo River	04.05.2017	0	0.09 ± 0.00	2.4 ± 0.0	22 ± 1.0	138 ± 4.2	10,827 ± 416	18.5 ± 6.8	2.0 ± 0.1	31.8 ± 9.2
	22.07.2017	0	0.09 ± 0.01	1.5 ± 0.4	19 ± 2.6	97 ± 7.6	6,689 ± 771	8.8 ± 2.4	0.8 ± 0.0	14.3 ± 5.3
	08.10.2017	0	0.07 ± 0.00	1.2 ± 0.2	9.9 ± 0.9	76 ± 4.1	4,638 ± 219	7.0 ± 0.6	0.5 ± 0.0	226 ± 23
	Mean ± sd	0	0.08 ± 0.01	1.7 ± 0.6	17 ± 6.3	104 ± 132	7,385 ± 3,153	11 ± 6.1	1.1 ± 0.8	91 ± 117
Coastal seawater[a]	28.11.2015	35.28	0.01 ± 0.00	0.04 ± 0.00	0.72 ± 0.01	2.6 ± 0.0	0.52 ± 0.01	2.1 ± 0.0	0.01 ± 0.00	0.06 ± 0.01[b]

[a]The Congo River water and coastal seawater (−8.2°S, 12.1°E) were used to produce two-endmember conservative mixing lines. [b]Dissolved Zn concentration is unavailable for the chosen coastal seawater sample, and therefore the dZn concentration of the closest sample with similar salinity was used.

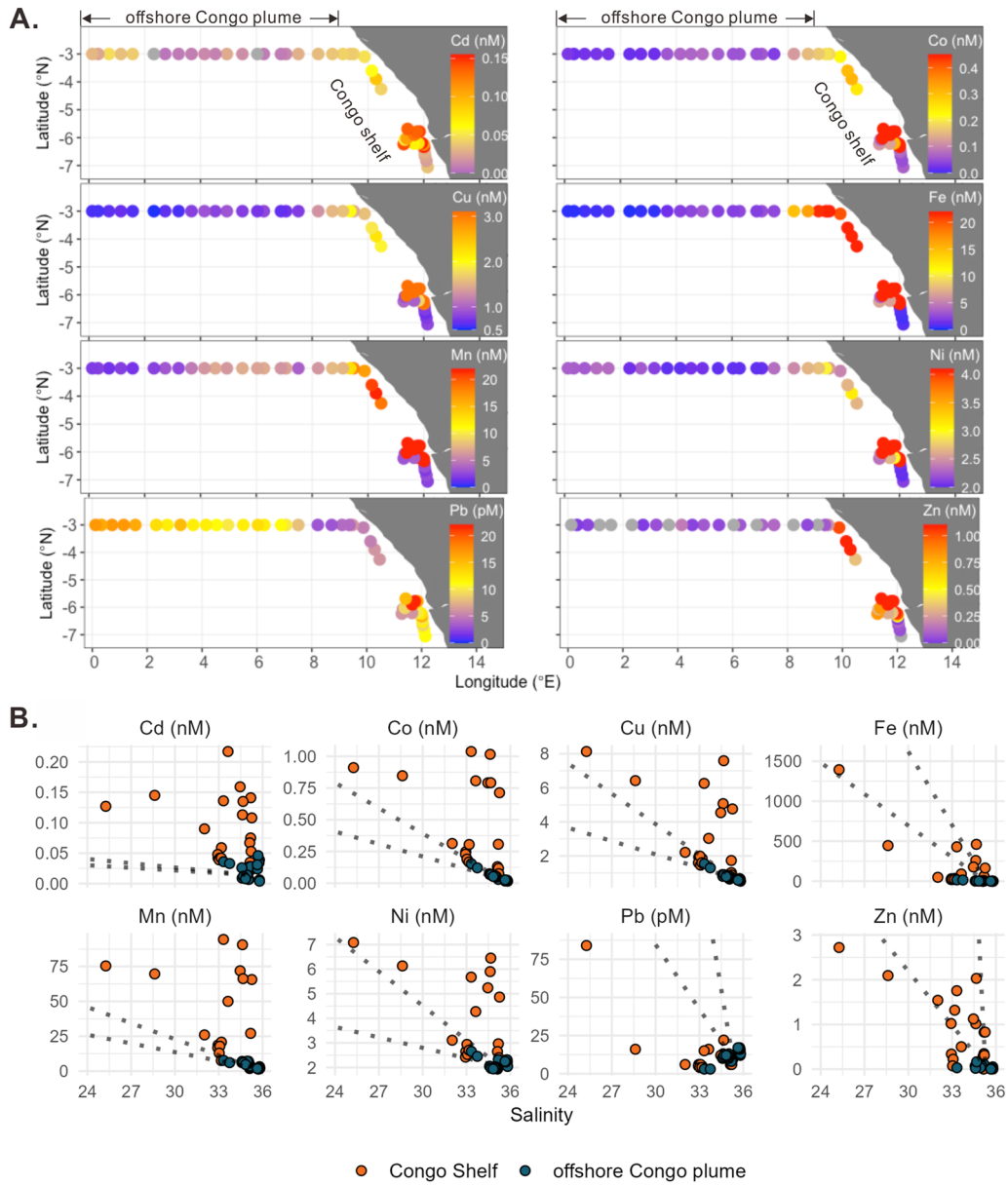

Figure 2. Concentrations of dTM in the study region affected by the Congo River plume. (a) Surface distributions of dissolved TM concentrations in the study region (colored dots). Two regions of interest, the Congo shelf and the offshore Congo plume are indicated in the top panel as defined in Figure 1. Data below detection limits is shown by gray dots. (b) Relationships between surface dissolved TM concentrations and salinity in the Congo shelf (orange circles) and offshore Congo plume (blue circles) of our study. Two dashed lines in each panel indicate theoretical conservative mixing lines associated with high and low measured Congo River endmembers (Table 1).

3. Results and Discussion

3.1. Impact of Congo River on Congo Shelf Waters and South Atlantic Ocean

Enhanced dTM concentrations were observed in surface waters on the Congo shelf (Figure 2a) and levels typically decreased with increasing salinity (Figure 2b), suggesting mixing of Congo River water with coastal waters with lower dTM levels (see Section 3.2). The Congo plume was detectable along an offshore transect of up to ~1,400 km from the river mouth into the South Atlantic subtropical gyre (Figure 1), with elevated surface dTM concentrations for elements such as Co, Cu, Fe and Mn (Figure 2). Gradients of decreasing concentrations of dCo, dCu, dFe and dMn with increasing salinity to the open ocean indicate offshore transfer of the Congo plume

(Figure 2). In contrast, the concentrations of Cd, Ni and Pb increased to ~0.05 nM, ~2.5 nM and ~20 pM, respectively (Figure 2), at the stations furthest west, and were similar to surface concentrations reported for the western South Atlantic (e.g., GEOTRACES GA02 cruise: 0.01 ± 0.02 nM of Cd, 2.9 ± 0.8 nM of Ni, 17 ± 5.2 pM of Pb) (GEOTRACES Intermediate Data Product Group, 2021). The increase of Cd, Ni and Pb moving offshore is due to high concentrations of these TMs in South Atlantic surface waters and suggests that the Congo plume is not likely a major source of these TMs.

The TM fluxes from the Congo River into the South Atlantic are shown in Figure 3a. Compared to other large river systems (Table S3 in Supporting Information S1), the Fe and Zn fluxes to the ocean from the Congo River are of a similar order of magnitude as those from the Amazon and the Orinoco rivers. Nevertheless, the Fe and Zn fluxes are almost two times higher from the Congo River than from the Amazon River despite of the lower discharge volume of the Congo River (~41,000 $m^3\ s^{-1}$) compared to the Amazon River (~20,5000 $m^3\ s^{-1}$, Gaillardet et al., 2014). This can be attributed to a low estuarine removal of Fe and anthropogenic Zn inputs, respectively (see Section 3.3-3.5). In addition, fluxes of Cd, Pb and Cu fluxes from the Congo River are at the high end of the range for large river systems, but similar as those from the Yangtze River, which is heavily impacted by anthropogenic activities (e.g., Wang et al., 2014).

The water column stratification in our study region will have concentrated the riverine TM inputs within the plume in the surface waters (Figure 2a and Figure S2 in Supporting Information S1), corroborated by depth profiles which show enhanced concentrations of dCo, dCu, dFe and dMn in the near-surface waters (Figure S5 in Supporting Information S1). Figure 3b shows the surface water inventories of dTMs, which are remarkably high for particle-reactive TMs including Cu, Fe, Mn and Zn. These elements are typically removed by scavenging and precipitation processes (e.g., Boyle et al., 1977; Mosley & Liss, 2020; Sholkovitz, 1978). The inventories allow the assessment of various external inputs to the surface ocean along the cruise track, which will be discuss in detail in Section 3.4.

3.2. Non-Conservative Addition of Trace Metals on the Congo Shelf

We created theoretical two-endmember conservative mixing lines for each TM using the observed Congo River dTM concentrations ($S = 0$, sampled in 2017) and a high salinity coastal surface water sample from ~8°S ($S = 35.28$, Table 1) that was not directly affected by the Congo River plume (Vangriesheim et al., 2009). All dTMs showed apparent non-conservative mixing behavior with respect to salinity on the Congo Shelf (Figure 2b). Concentrations of dCd, dCo, dCu, dMn and dNi fell above their conservative mixing lines across the whole salinity gradient between the Congo River and coastal waters. Apparent removal of dFe and dPb at salinity <33, and dZn at salinity <30 is consistent with their characteristic scavenging behavior. These TMs typically exhibit non-conservative removal in estuaries (Boyle et al., 1977; Elderfield et al., 1979; Krauskopf, 1956; Mosley & Liss, 2020; Sholkovitz, 1978). However, weaker and insignificant correlations between dTMs and distance from the river mouth (Pearson coefficient $R < 0.45$, $P > 0.05$) could suggest the river was not the only major source for all dTMs on the Congo shelf (Table S5 in Supporting Information S1). River water was collected in a different year (2017) to the cruise (2015), and therefore an apparent "missing" source could be due to river water concentration for all dTMs in 2017 being much lower than in 2015. However, dTM concentrations in Congo River waters in the wet season (October to December) are lower than in the dry season (April to June) (Table 1 and Figure S3 in Supporting Information S1), as increases in discharge volume generally dilute estuarine dTM concentrations (Braungardt et al., 2003). Concentrations of dCd, dCo, dCu, dMn and dNi on the Congo shelf are higher during the wet season than their highest theoretical conservative values created using dry-season river concentrations (from May 2017, Table 1). The observation that TMs are consistently elevated above the theoretical mixing line thus suggest other dTM sources in addition to river water (Figure 2b). This was also suggested in prior work from the same cruise using ^{228}Ra for budget assessments. ^{228}Ra shares the same source as TMs like Fe, Mn and Co, and indicated that the Congo River accounted for only ~30–35% of the ^{228}Ra budget in the plume (Vieira et al., 2020).

Although several mechanisms with different strengths may simultaneously deliver TMs to the Congo shelf, the surface-advected Congo plume disconnects from the seafloor on the shelf immediately beyond the river outflow (Hopkins et al., 2013) and is strongly stratified with an upper layer about 15 m deep and ~3.0 psu fresher than subsurface waters (Figure S2 in Supporting Information S1). The stratified water column and low wind speeds (<10 $m\ s^{-1}$, Figures S1 and S2 in Supporting Information S1) on the Congo shelf reduced vertical mixing and upwelling, thereby limiting the transfer of TMs between subsurface and surface waters. The water column

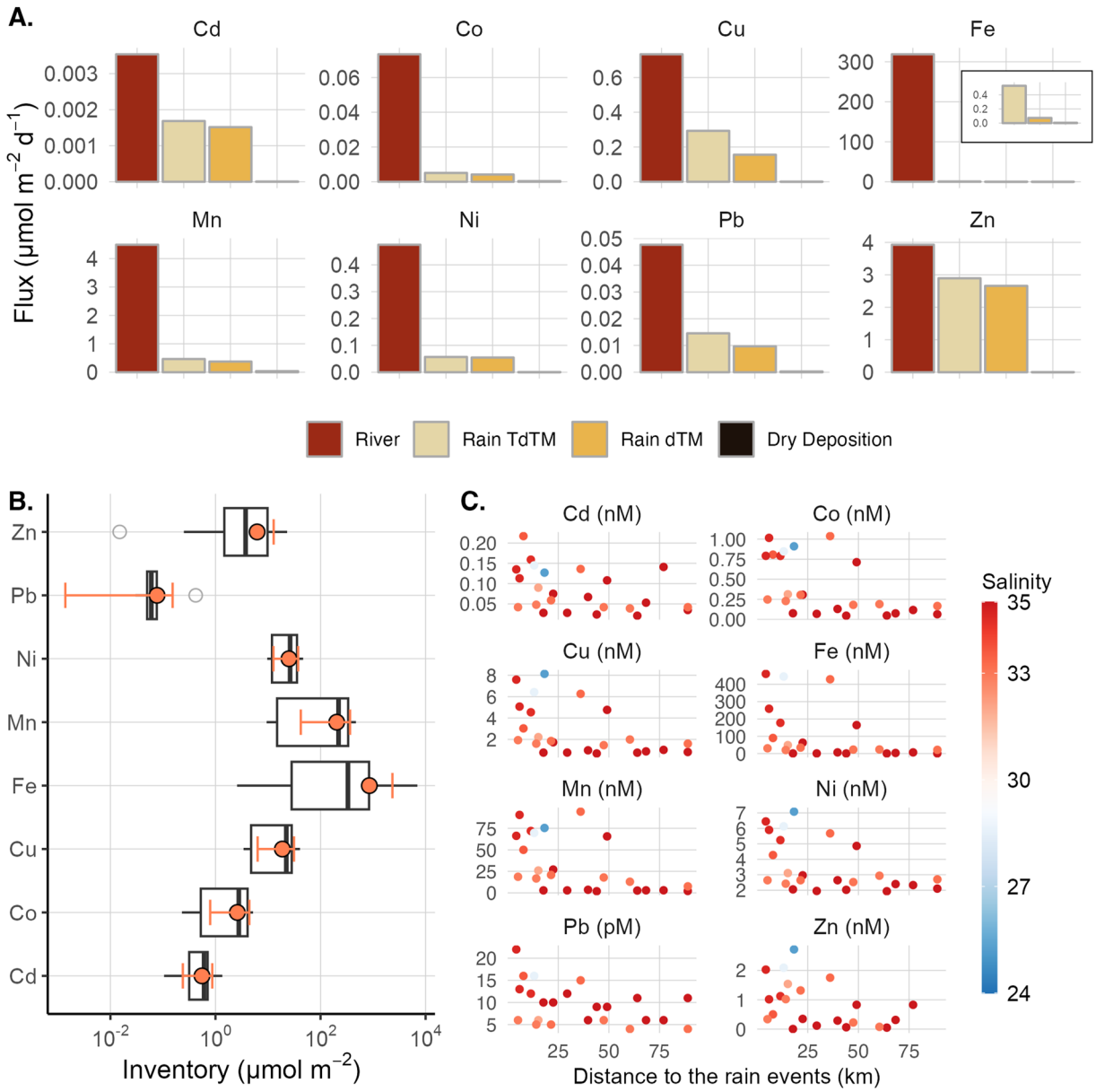

Figure 3. Fluxes and inventories of TMs and TM distribution with respect to the area receiving high rainfall on the Congo shelf. (a) TM fluxes (μmol m^{-2} day^{-1}) from the Congo River (River), rainfall (total dissolvable: Rain TdTM and dissolved: Rain dTM) and atmospheric dry deposition (Dry Deposition). In-set shows Fe fluxes from Rain TdTM, Rain dTM, and Dry Deposition. (b) TM inventory (μmol m^{-2}) in surface water along transect on the Congo shelf. Note the log scale. Boxes represent median values, 25th and 75th percentiles. Gray points outside boxes are potential outliers which are defined as above the 75th or below the 25th percentile by a factor of 1.5 times the interquartile range. Orange points represent mean values of each TM inventory with error bar (1sd). (c) Dissolved TM concentrations on the Congo shelf plotted against distance from discrete rain events (km) with colors showing salinity during the cruise. Note that data in A and B as per Table S4 in Supporting Information S1. In C, concentrations of dissolved TMs are in nM except Pb in pM. Position of rain events is shown in Table S1 in Supporting Information S1. One datapoint with the highest Pb (84 pM) and Fe (1,394 nM) concentrations and lowest salinity ($S = 25.3$) is not shown.

structure of the Congo plume, and the observed vertical distribution of dTMs with lower dTM concentrations in subsurface compared to surface waters (Figure S5 in Supporting Information S1), therefore suggest that shelf sediments were not a major dTM source to the surface layer. This observation for the Congo plume is in contrast to reported benthic dTM inputs in other shelf systems, which typically result in a general trend of increased dTM concentrations toward the seafloor (Liu et al., 2022b; Noble et al., 2012). For dFe and other TMs with similar sources in the plume, a minimal impact of lithogenic input from the Congo shelf is substantiated by heavier Fe isotopic compositions (δ^{56}Fe > +0.33‰, up to ~+1.2‰) in Congo plume waters relative to both the typical

Table 2
Comparison of Endmembers and Fluxes Between a Linear Regression Model (LM), General Additive Model (GAM) and Calculations Based on Ra Isotopes (Vieira et al., 2020)

	LM ($S = 0$)		GAM ($S = 0$, distance to the river mouth = 500 km)		Ra-derived[a]
TM	Endmember (nM)	Flux (mol day^{-1})	Endmember (nM)	Flux (mol day^{-1})	Flux (mol day^{-1})
Co	1.84 ± 0.08	$6.6 \pm 1.9 \times 10^3$	2.93 ± 0.84	$1.1 \pm 0.4 \times 10^4$	$1.3 \pm 0.5 \times 10^4$
Cu	12.7 ± 1.00	$4.6 \pm 1.3 \times 10^4$	20.1 ± 2.02	$7.2 \pm 2.1 \times 10^4$	$8.5 \pm 3.8 \times 10^4$ [a]
Fe	204 ± 25.7	$7.3 \pm 2.1 \times 10^5$	99.4 ± 14.3	$3.6 \pm 1.1 \times 10^5$	$1.9 \pm 0.6 \times 10^6$
Mn	97.2 ± 16.4	$3.5 \pm 1.1 \times 10^5$	182 ± 52.8	$6.6 \pm 2.6 \times 10^5$	$8.5 \pm 3.3 \times 10^5$

[a]From Vieira et al. (2020), a Ra-derived Cu flux was calculated as previously undertaken for Co, Fe and Mn.

crustal δ^{56}Fe values (~+0.1‰) (Fitzsimmons & Conway, 2023) and to the subsurface benthic Fe(II) inputs associated with low O_2 (Hunt et al., 2022). Additionally, the δ^{56}Fe signatures in the plume cannot be explained by a simple closed-system Rayleigh fractionation induced for example, by removal processes during mixing of river and seawater (Hunt et al., 2022). Internal cycling and a net dissolution of TMs from riverine particles therefore did not likely act as a large net dFe source within the plume. This is consistent with the rapid and efficient net transfer of dFe to particulate phases in estuaries and previous observation during mixing in the Congo estuary (Boyle et al., 1977; Figuères et al., 1978; Sholkovitz, 1978). Altogether, these observations combined with TM distributions on the Congo shelf suggest additional external sources of TMs other than the Congo River and shelf sediments.

3.3. Trace Metals Delivered by Wet Atmospheric Deposition

The Congo shelf experienced numerous heavy rain events during our cruise, with precipitation rates of >1 mm hr^{-1} as confirmed by satellite data (Figure 1 and Figure S1 in Supporting Information S1). We thus consider wet deposition as a potentially important source of TMs to surface waters as reported for other ocean regions (Desboeufs et al., 2022; Schlosser et al., 2014). As a result of the episodic and dispersed nature of rain events, it is challenging to decouple rain from river inputs of dTMs. Observed enhanced TM concentrations on the Congo shelf (dCd >0.51 nM, dCo >0.25 nM, dCu >1.73 nM, dFe >21.4 nM, dMn >12.5 nM, dNi >2.65 nM, dPb >5 pM and dZn >0.35 nM) typically were in proximity to rain events, notably within 25 km (two datapoints within 25–50 km) from rainwater sampling locations (Figure 3c). For the interpretation of the potential effects of recent rainfall on dTM distributions it should be noted that the underway salinity observations on the vessel were conducted at a depth of ~2.5 m, whilst the intake of water for TM analysis using the tow fish was at a depth of 1–2 m. This may have resulted in an increased uncertainty with respect to TM-salinity relationships considering the strong salinity gradients in the top few meters of the water column. Towfish dTMs collected herein therefore may have a weaker relationship with salinity than would have been observed if the salinity of individual samples were determined.

Over short time periods, rainwater deposition would be expected to increase concentrations in surface waters of scavenging-type dTMs (e.g., dFe) and this input would be evident despite the fact that the rainwater concentrations are lower than river water concentrations. This is because dTM concentrations in the plume are measured subsequent to the estuarine removal processes. A dTM enrichment could occur from rainwater when the rainwater concentration is higher than the apparent freshwater endmember, which may be considerably lower than the measured freshwater endmember. This is particularly the case for dFe where apparent freshwater endmembers in estuaries are almost invariably 1–2 orders of magnitude lower than measured riverwater concentrations (Boyle et al., 1977) ($dFe_{measured}$ = 7,385 nM v.s. $dFe_{derived}$ = 204 nM in this study) (Tables 1 and 2).

We calculated volume-weighted-mean TM concentrations in rainwater (Table S6 in Supporting Information S1) to avoid the volume effects whereby heavy rain events tend to exhibit progressively lower TM concentrations with increasing rain volume (Figure S4 in Supporting Information S1). Our volume-weighted-mean concentrations of all TMs in rainwaters were within the range of those reported in studies worldwide (Baker et al., 2013; Chance et al., 2015; Desboeufs et al., 2022; Shelley et al., 2017), with Cd, Cu, Mn, Pb and Zn at the higher end and Co and Fe at the lower end. Specifically, higher rainwater Cd, Cu, Pb and Zn concentrations were reported for the South Atlantic (Chance et al., 2015) (including this study) compared to the North Atlantic Ocean (Baker et al., 2013;

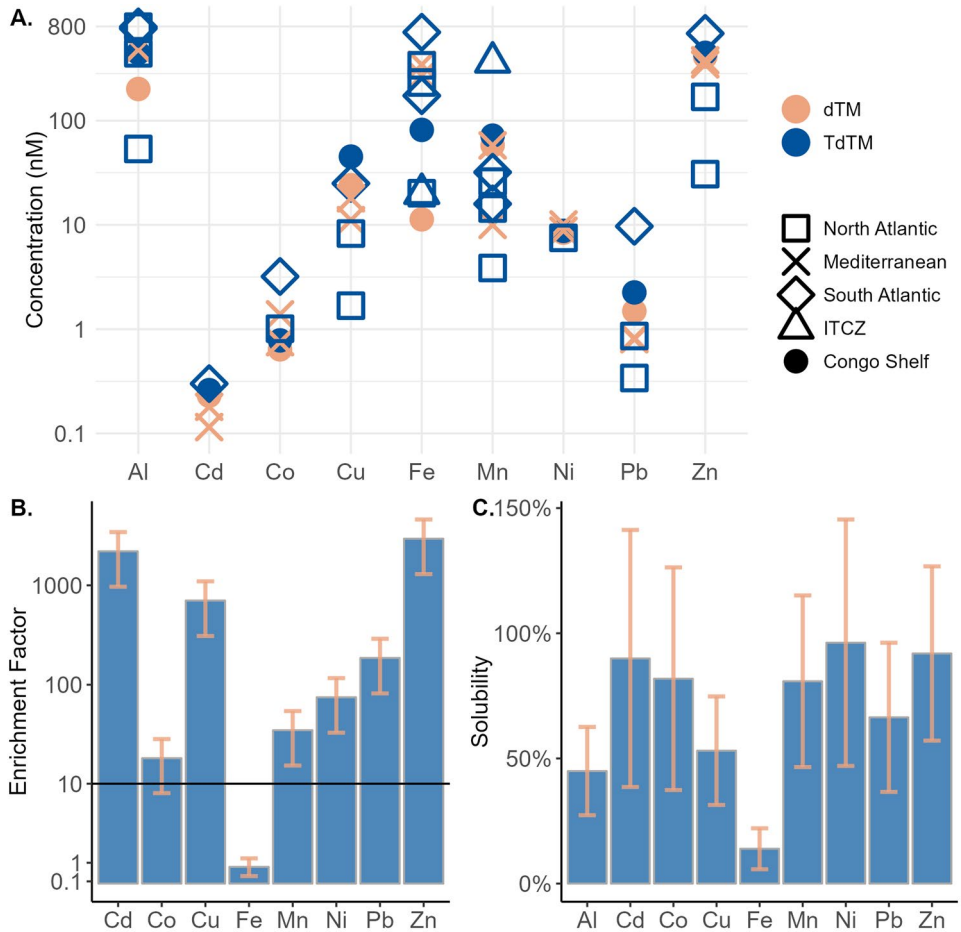

Figure 4. Trace metal concentrations in rainwater. (a) Volume-weighted-mean dissolved (dTM, orange) and total dissolvable (TdTM, blue) TM concentrations (log scale) in different areas including the North Atlantic (Baker et al., 2013; Shelley et al., 2017) (squares), Mediterranean (Desboeufs et al., 2022) (crosses), South Atlantic (Baker et al., 2013; Chance et al., 2015) (diamonds), ITCZ (Baker et al., 2013) (triangles) and the Congo shelf (this study, circles). (b) Enrichment factor (EF, log scale) and (c) fractional solubility (solubility). Error bars of EF and solubility were derived by error propagation of volume-weighted-mean concentrations for each metal. Black horizontal line in B denotes EF = 10, representing a significant enrichment of TMs relative to upper continental crust. Data as per Table S6 in Supporting Information S1. Note the log scale for concentrations in panel A and Enrichment Factor in panel B all rainwater TM concentrations from literature are volume-weighted-mean concentrations, whereas data from the Mediterranean refers to two individual samples (Desboeufs et al., 2022).

Shelley et al., 2017) (Figure 4a), likely reflecting different regional sources of the TMs. Rainwater Fe concentrations in our study area were around one order of magnitude lower than those in most areas of the northern hemisphere (Baker et al., 2013; Shelley et al., 2017), but similar to observations in the intertropical convergence zone (ITCZ) (Baker et al., 2013) with high rainfall, and in the western high-latitude North Atlantic (~60°N) (Shelley et al., 2017). Concentrations of most TMs in rainwaters in our study, including Cd, Co, Cu, Mn, Ni, Pb and Zn, were similar to those reported for the central and western Mediterranean Sea (two individual samples), where wet deposition is influenced by high dust loading and anthropogenic emissions (Desboeufs et al., 2022). However, Fe concentrations were lower by a factor of ~20 compared to the Mediterranean study (Desboeufs et al., 2022). The difference is perhaps related to the enhanced dust loadings in the Mediterranean Sea region, derived from the Sahara and Sahel areas (Baker et al., 2013; Nickovic et al., 2013; Sedwick et al., 2007) and/or low Fe concentrations of pyrogenic aerosol from South Africa (Barkley et al., 2019; Sholkovitz et al., 2012).

Enrichment Factors (EF) are used as indicators of a non-crustal source of anthropogenic TM emissions and, whilst inherently variable, EFs >10 provide relatively strong evidence for anthropogenically perturbed atmospheric inputs with the natural ratio being exceeded by over an order of magnitude (Nriagu, 1979). All TMs except Fe were significantly enriched relative to mean upper continental crust (UCC, Rudnick & Gao, 2014), with Co

showing the next lowest enrichment (EF = 18.2) and Zn the highest (EF = 2,942). The EFs thereby indicate non-crustal sources for almost all measured TMs (Figure 4b). Low EF values of Fe (<10, specifically, 0.79 relative to the UCC and 0.20 relative to Namibian dust, Eltayeb et al., 1993) indicate Fe in rainwater is mainly associated with mineral dust. However, an anthropogenic influence on Fe is possible due to a similar fractional solubility in rainwater (hereafter referred as solubility) for Fe (14%) as global simulated 9.1%–22% water-soluble Fe from anthropogenic sources (Ito & Miyakawa, 2022), which is higher than the typical fraction of water-soluble Fe in lithogenic aerosol particles (<10%) (Desboeufs et al., 2005; Ito et al., 2019).

The solubility of Al (45%) in our study was higher than the reported median Al solubility of 13% (Baker et al., 2013). This is likely due to the more acidic nature (pH ~4.3–5.0, Table S1 in Supporting Information S1) of our rain events compared to typical rainwaters (pH ~5.0–5.6), despite comparable solubilities of Fe (14%) and Mn (81%) in our study to reported median values of 9.4% and 74%, respectively, based on compiled Atlantic data (Baker et al., 2013). Aluminum minerals (e.g., aluminosilicates) release more Al at pH ~4.75 and below (Johnson et al., 1981; Lim et al., 1994; Losno et al., 1993), whereas Fe in dust was reported to show enhanced dissolution at pH < 3.6 (Mackie et al., 2005). The pronounced enrichment of Cd, Cu and Zn (up to 10^3 for Cd and Zn) likely reflects increased solubilities in rainwaters related anthropogenic sources as also reported for other regions (Figure 4) (Desboeufs et al., 2022; Shelley et al., 2017). The anthropogenic perturbation of TMs in rainwater is not surprising due to air pollution over West Africa (Knippertz et al., 2015), but few studies have reported on emission inventories from specific regional activities. These activities include extensive hydrocarbon exploitation (Figure S2 in Supporting Information S1, Global Gas Flaring Reduction Partnership, 2020), metal mining, marine traffic and biomass burning. Therefore, it is challenging to constrain specific dTM signatures other than a generalization that elements such as dZn and dPb are most impacted by anthropogenic perturbations (Boyle et al., 1994; Graedel et al., 2005).

3.4. River and Rainfall Contributions to Surface Trace Metal Inventories

We compare TM inputs from the Congo River, rainwater and dry atmospheric deposition with respect to surface water TM inventories on the Congo shelf (Figure 3). Atmospheric dry deposition of each TM was calculated based on an Al-derived dust deposition flux (2.67 g m^{-2} yr^{-1}) to the Congo shelf (Barraqueta et al., 2019) assuming a similar TM abundance as the UCC (Rudnick & Gao, 2014) and using the experimental solubility of aerosols (Mackey et al., 2015) (Text S2 in Supporting Information S1). The inputs from the Congo River were highest for all TMs followed by those from rainfall, which are 1–3 order of magnitude higher than dry deposition. This could be due to the washout effect of rain (Jickells et al., 1984; Vink & Measures, 2001) and/or an underestimation of TM dry deposition fluxes by assuming a TM content is similar to the UCC (Text S2 in Supporting Information S1). Comparing the TM inventories and inputs (Figure 3), Fe, Pb and Zn have notably short residence times (<3 days, Table S4 in Supporting Information S1) which is consistent with their scavenged-type behavior. Cadmium, Co, Cu, Mn and Ni have longer residence times (18–106 days, Table S4 in Supporting Information S1), reflecting enhanced inventories compared to riverine inputs and atmospheric deposition (Figure 3).

Rainfall supplies Cd, Cu, Pb and Zn at similar magnitudes to the Congo River (Figure 3a). The relative importance of rainfall calculated herein is likely underestimated by our calculations, as a fraction of the TMs in the Congo River also likely originated from inputs of rain to the catchment (Best, 2019). Rainfall inputs account for at least ~60% of Pb and >100% of Zn inventories over the period of surface water residence times (~2.7 days) on the Congo shelf (Eisma & Van Bennekom, 1978), suggesting a considerable impact of anthropogenic inputs. Wet deposition supply of dTMs (Rain dTM) is equivalent to 0.02%–68% of river inputs with the relative importance of rainfall as a dTM source decreasing in the order Zn > Cd > Cu > Pb > Ni > Mn > Co > Fe (Figure 3a). Whilst wet deposition was therefore a major feature of some dTM budgets in the Congo plume (e.g., Zn, Pb and Cu), consistent with inferences that there are large dTM sources other than the Congo river and shelf sediments, the relatively low contribution of wet deposition to some of the other elements with apparent missing sources (e.g., Mn, Co and Fe) suggests that there are still other missing sources or limitations in the assumptions used to construct budgets to date.

3.5. Freshwater Trace Metal Fluxes to the South Atlantic Ocean

We used two models (Table S7 in Supporting Information S1), a linear regression (LM, TM concentrations against salinity) and a non-linear general additive model (GAM, TM concentrations against distance to river mouth and salinity), to derive freshwater dTM endmembers at the on-set of the offshore Congo plume (salinity = 0 and distance to the river mouth = 500 km, Figure 1) (Krisch et al., 2021; Wood, 2017). Correspondingly, freshwater TM fluxes were computed (Text S2 in Supporting Information S1) using the two respective freshwater endmembers (LM-extrapolated

and GAM-predicted). The differences between LM-extrapolated and GAM-predicted endmembers can be attributed to various modifications on the shelf including scavenging, phytoplankton uptake and addition from atmospheric inputs. Differences between the derived TM fluxes using the two endmembers thereby represent net additions or loss of TM fluxes in the freshwater plume. The GAM-predicted freshwater endmembers of Co, Cu and Mn at the beginning of the offshore Congo plume (2.93 ± 0.84 nM dCo, 20.1 ± 2.02 nM dCu, 182 ± 52.8 nM dMn) are significantly higher than the LM-extrapolated freshwater endmembers (1.84 ± 0.08 nM dCo, 12.7 ± 1.00 nM dCu, 97.2 ± 16.4 nM dMn, Table 2), consistent with additions of Co, Cu and Mn on the Congo shelf. In contrast, the lower GAM-predicted freshwater Fe endmember (99.4 ± 14.3 nM) compared to the LM-extrapolated freshwater value (204 ± 25.7 nM) indicates a net 51 ± 21% loss of Fe during transfer after estuarine removal (Table 2). The lower Fe loss (51 ± 21%) compared to previous observations of ∼85% determined at low salinities in the Congo estuary (Figuères et al., 1978) could be related to other shelf sources such as rainwater additions, which perhaps compensated for at least a fraction of apparent Fe removal on the Congo shelf. This notion is supported by a much lower removal factor (∼17%) of dFe in mixing experiments between freshly collected rainwater and seawater (Kieber, Willey, & Avery, 2003) which indicated that rain-derived dFe is stable on timescales of hours upon mixing likely due to a high fraction of Fe(II) produced by photochemical reactions in rain droplets (Kieber, Hardison, et al., 2003) and/or the presence of organic matter complexing Fe in rain (Kieber et al., 2001, 2005). The specific nature of organic matter in the Congo plume has been proposed to contribute to the efficient distal transport of Fe offshore (Hunt et al., 2022; Vieira et al., 2020). Such a mechanism of organic matter complexation may also buffer against scavenging and removal of dCo and dCu in the distal plume (Jacquot & Moffett, 2015; Saito & Moffett, 2001).

Strong correlations between most dTMs, ^{228}Ra and salinity suggest a major freshwater source of most elements, although this could also reflect entrainment of other coastal sources into the plume close to its origin. It is plausible that submarine groundwater discharge, net release of dTMs from shallow near-shore shelf sediments and dissolution of riverine material could also contribute significant loads of dTMs and remain tightly correlated to ^{228}Ra and salinity over the off-shelf transect. However, such sources would have to be delivered in a way that they remained confined to the low salinity surface layer, and for some elements several of these sources are implausible. For example, dissolution of riverine particles is not usually found to constitute a large net-source of scavenged-type elements in estuaries at low salinities (Boyle et al., 1977; Figuères et al., 1978; Sholkovitz, 1978). Considering the absence of a sedimentary signal in the Fe isotopic data (Hunt et al., 2022), submarine groundwater released into shallow areas of the Congo shelf therefore possibly forms the next most plausible explanation to rainwater, for why TMs show missing sources in the Congo plume. This could also perhaps similarly explain the apparent discrepancies in Co and Mn budgets and warrants further investigation.

4. Conclusions and Implications

The Congo River forms a major source of TMs to the South Atlantic Ocean. Following earlier studies implicating an additional source of TMs to the Congo plume other than the Congo River and shelf sediments (Hunt et al., 2022; Vieira et al., 2020), our study indicated regional wet deposition across the Congo shelf as a TM source to the Congo plume. Concentrations of TMs in rainwater in our study are all within the range of global reported values and similar to those from the North Atlantic and the Mediterranean Sea (Desboeufs et al., 2022; Shelley et al., 2017). Our results suggest that wet deposition contributes to Cd, Cu, Pb and Zn fluxes to the Congo shelf on the same order of magnitude as the Congo River, with minor contributions to Fe, Mn and Co. Considering the observed enhanced residence time of TMs in the distal Congo plume toward the open ocean, wet deposition of TMs to the surface ocean maybe partly responsible for a longer longevity of some elements in the plume, with potential consequences for ocean productivity.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Dissolved TM and macronutrient concentrations from the GA08 cruise are archived at Pangaea (Liu et al., 2022a).

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