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Effects of agricultural land use on the composition of fluvial dissolved organic matter

Henry F. Wilson[1]* and Marguerite A. Xenopoulos[2]*

Nearly 40% of the Earth's ice-free surface area is cropland or pasture[1]. Agricultural land use can increase the delivery of nutrients such as nitrogen and phosphorus to fluvial ecosystems[2], but the impact of farming on riverine dissolved organic carbon is still largely unknown, despite increasing recognition that rivers act as important modifiers in the global carbon cycle[3,4]. Here, we examine the character of riverine dissolved organic matter in 34 watersheds along a gradient of agricultural land use. We show that changes in the character of dissolved organic matter are related to agricultural land use, nitrogen loading and wetland loss. Specifically, we find that the structural complexity of dissolved organic matter decreases as the ratio of continuous croplands to wetlands increases. At the same time, the amount of microbially derived dissolved organic matter increases with greater agricultural land use. Furthermore, we find that periods of soil dryness are associated with a decrease in the structural complexity of dissolved organic matter. We suggest that these effects of land use and climate on the character of riverine dissolved organic matter have important implications for global carbon cycling, owing to their potential to control rates of microbial carbon processing (for example, uptake, retention and outgassing) in agricultural systems.

Agricultural land use has led to significant increases in the export of riverine dissolved inorganic carbon[5], but despite the importance of rivers in the global movement of carbon, there have been few studies quantifying land use effects on the transport, concentration and quality of organic carbon. Agricultural land use seems to have variable effects on the concentration and export of organic carbon[6–8]. Some studies have hinted that agricultural systems export compounds of lower molecular weight[6], but a more extensive change in chemical dissolved organic matter (DOM) character with land use has not been demonstrated. With reference to overall carbon inputs to aquatic systems, DOM represents the largest and most bioavailable pool[3]. Microbial metabolism of DOM in streams acts as an important energy source[9] and could strongly influence carbon cycling by controlling rates of carbon uptake, retention and outgassing[3]. In most streams, DOM largely originates from terrestrial sources; however, it can also enter streams through carbon fixation and subsequent exudation by in-stream metabolism. As a result, the structural composition of a stream's DOM pool is defined by its origin. The use of DOM as a microbial energy source is controlled by the concentration of limiting nutrients[10], temperature[11] and the chemical composition of the DOM (refs 12–14). Therefore, if we hope to predict the dynamics of DOM transported from stream ecosystems, it is crucial that we understand the factors controlling its availability and character.

We examined the influence of agricultural land use on stream and river DOM character using absorbance and fluorescence spectroscopy. We compared the character of DOM in 34 temperate watersheds across a gradient of agricultural land use (1–76%) in Ontario, Canada. We applied four indices of general DOM structure: fluorescence index[15], molar absorption coefficient at 280 nm (E280; ref. 16), a humification index[17] and a ratio of two known fluorescing components[18] (β/α, where β represents more recently derived DOM and α represents highly decomposed DOM). The fluorescence index is commonly used to differentiate microbial from terrestrial sources of DOM (refs 15,19) and shows strong correlation with important features of the DOM skeleton: particularly per cent aromaticity[15] and degree of structural conjugation[20]. E280 values are also commonly used in characterizing DOM because of their strong correlation with aromaticity and molecular weight[16,21]. The humification index is associated with the condensing of fluorescing molecules and lower H/C ratios[17]. The ratio of β/α is an indicator of autochthonous inputs and when applied to our data set provides an indication of the relative contribution of recently microbially produced DOM (ref. 18). Fluorescence index and β/α values increase with increasing autochthonous carbon production, whereas high E280 and humification index values are an indication of humicity. The relationships of these indicators to water chemistry and watershed landscape were quantified using water samples collected nine times over two years, encompassing both high- and low-discharge conditions.

We found that DOM character in streams and rivers can be significantly influenced by agriculture land use (Fig. 1, Table 1). The fluorescence index and β/α values increased significantly with the proportion of continuous cropland, indicating a more microbially derived DOM character (Fig. 1). Relationships predicting DOM character were slightly stronger with riparian land use; however, entire watershed and riparian land uses were highly correlated (for example, continuous cropland, $r = 0.88$). This shift in DOM character was probably driven by increased availability of nitrogen to the microbial community. Related to this, we found a strong positive relationship between continuous cropland and total dissolved nitrogen (TDN; Table 1), but not phosphorus. Given that experimental nitrogen additions have been associated with both increased bacterial production[10] and release of chromophoric DOM (ref. 22), the strong relationship between TDN and β/α (Fig. 1f) probably indicates a nutrient-induced increase in autochthonous DOM production (Fig. 1).

Although nitrogen enrichment is a probable mechanism for the increased production of more autochthonous DOM in agricultural streams, we cannot rule out other potentially important land use

[1]Watershed Ecosystems Graduate Program, Trent University, Peterborough, Ontario, K9J 7B8, Canada, [2]Department of Biology, Trent University, Peterborough, Ontario, K9J 7B8, Canada. *e-mail: henrywilson@trentu.ca; mxenopoulos@trentu.ca.

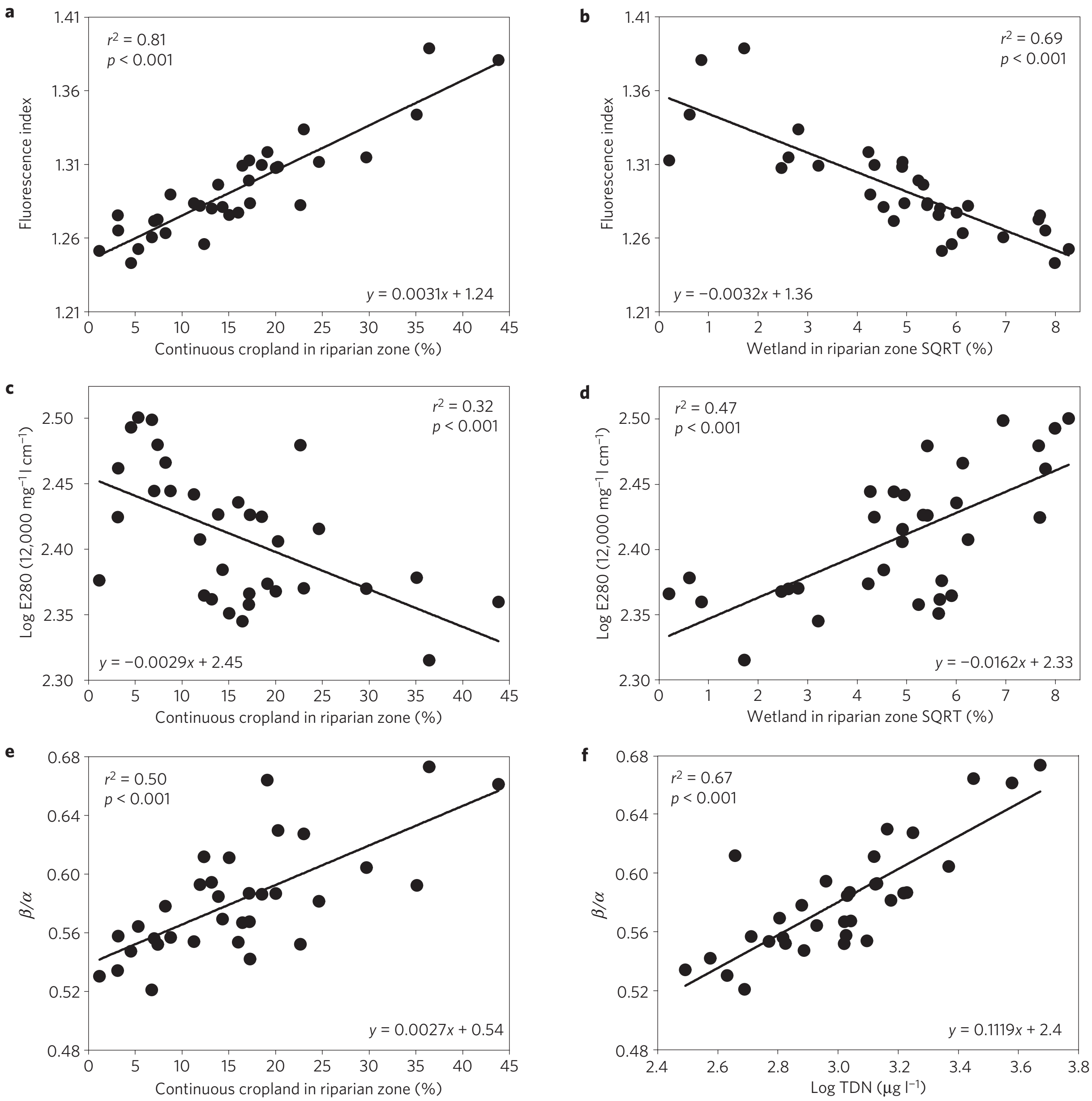

Figure 1 | Relationships between three indices of DOM character and landcover or nutrients. a–f, The best predictors for fluorescence index (**a**,**b**), molar absorption coefficient at 280 nm (E280) (**c**,**d**) and the ratio of components β/α (**e**,**f**). Shown are selected univariate linear regressions with the highest r-squared. Variables were either log or square-root transformed before analysis to meet the assumption of normality when needed.

processes. Specifically, it is also possible that the optical character of DOM exported from agricultural land is structurally less complex. Indeed, pore-water DOM in soils under continuous tillage tends to show lower molecular weights[23,24] and less humicity[13] than DOM in soils under native vegetation types. Further studies are needed to address the mechanisms that primarily drive the greater quantity of microbial-like DOM in agricultural streams.

When we examined the other indicators of DOM character, E280 and humification index values increased significantly with the proportion of wetlands in the watershed (Fig. 1, Table 1), a trend consistent with the observation that wetlands are often associated with humic and more structurally complex DOM (refs 19,25). As catchments with more continuous cropland have fewer wetlands ($r = -0.81$, $p < 0.001$), these land use patterns are related; however, the weaker relationships between E280, humification index values and continuous croplands compared with those for fluorescence index or β/α strongly suggest that fluorescence index, β/α, E280 and humification index indices are describing slightly different aspects of the DOM structure.

The three-dimensional (3D) excitation–emission matrices (EEM) of stream samples had characteristic humic-like peaks at Ex/Em 310–330/420–430 nm (α) and Ex/Em 250/420–435 nm (α'). In sites with more continuous cropland, these humic-like peaks were shifted to the lower end of these emission wavelengths (Fig. 2). A protein-like peak in the Ex/Em 280/350 nm (δ) EEM region has been associated with both macro-algal exudates[18] and bacterial activity from sewage- and manure-related organic pollution[26]. This peak was not very visible in our samples, but its presence was probably masked by both the large humic-like peaks that we observed[26] and by the rapid degradation of protein-like DOM by stream microbial communities[18]. A second microbially related peak in the Ex/Em 300–310/380–420 nm range (β) has been associated with both the degradation of the δ component[18] and plankton productivity[27] (see Supplementary Information, Fig. S1).

Table 1 | Stepwise regression models predicting stream DOM character, export, water yield, chemistry and DOC across a gradient of land use.

Variable	RSQ	Model
Fluorescence index	0.86	$= 1.28 + 0.0022$ (riparian continuous cropland) $- 0.0050$ ($\sqrt{}$ riparian wetland)
logE280 (12,000 $mg^{-1}\,l\,cm^{-1}$)	0.80	$= 1.80 + 0.016$ ($\sqrt{}$ riparian wetland) $+ 0.016$ (riparian rural) $- 0.031$ (log area)
β/α	0.86	$= 0.37 + 0.045$ (log TDN) $+ 0.0012$ (total riparian agriculture) $+ 0.002$ (chlorophyll a) $+ 0.017$ (log area)
Humification index	0.57	$= 16.8 - 3.01$ (log area) $+ 0.79$ ($\sqrt{}$ riparian wetland) $+ 0.12$ (riparian rural)
Log mean 9-month export (tons)	0.83	$= 2.99 + 0.935$ (log area) $+ 0.094$ ($\sqrt{}$ wetland)
Mean 9-month water yield – log (m^3)	0.70	$= 5.02 + 0.954$ (log area)
logDOC ($mg\,l^{-1}$)	0.78	$= 1.06 - 0.39$ (log riparian wooded) $+ 0.056$ ($\sqrt{}$ poorly drained soil)
logTDN ($mg\,l^{-1}$)	0.52	$= 2.69 + 0.020$ (riparian continuous cropland)
Chlorophyll a ($\mu g\,l^{-1}$)	0.48	$= -32.7 + 21.42$ (log total dissolved phosphorus) $+ 6.17$ (log TDN)

Predicted variables represent averages taken across nine sampling dates and when needed, were either log or square-root transformed to meet normality. All final models had p values <0.001 ($n = 34$). Percentages were used as units for landcover and square kilometres for area. Fluorescence index, humification index and β/α are dimensionless. Units are given for other predicted variables RSQ, R-squared.

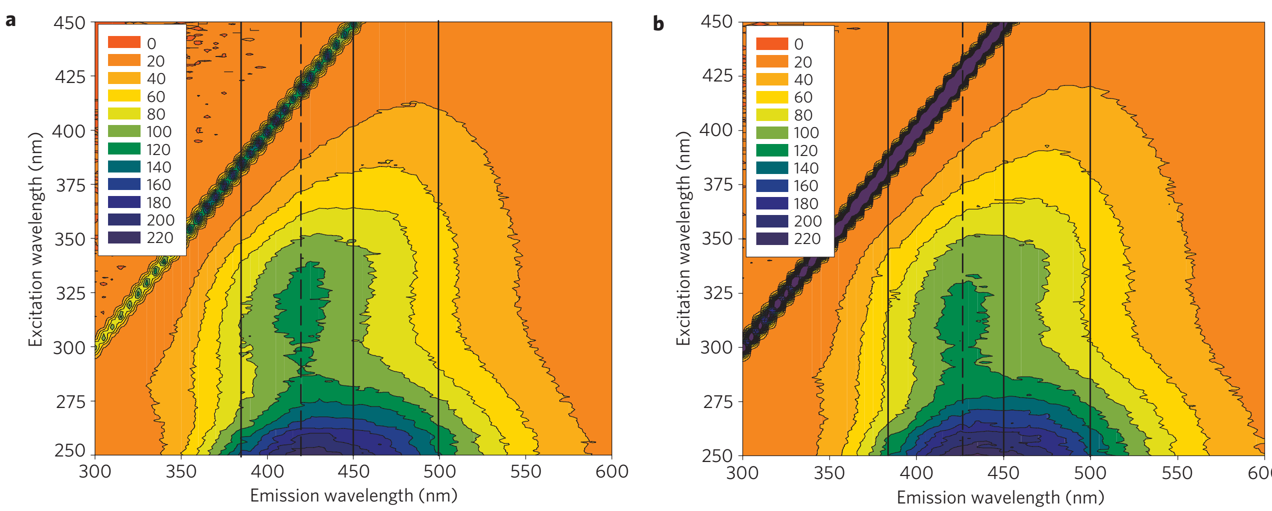

Figure 2 | Changes in fluvial DOM character with proportion of cropland in the watershed. a,b, Examples of 3D EEMs for a watershed with high continuous cropland (**a**) and low continuous cropland (**b**). The solid lines denote the emission wavelengths used in the calculation of β/α and the fluorescence index and are placed at emission wavelengths of 380 nm, 450 nm and 500 nm; the dashed line represents the maximum emission wavelength for the α component.

Our results show that the ratio of β to α is strongly controlled by factors that could be expected to stimulate microbial activity, particularly nitrogen.

When we examined indicators of aromaticity (E280, humification index) and their relationship with landcover, we found a large amount of variation between sampling dates that was not explained by land use, but was strongly correlated to long-term climatic conditions calculated using the Palmer Drought Index. This index uses a water balance approach and provides an indication of the deviation of long-term soil moisture conditions from average conditions[28]. When considering streams individually, measured seasonal Palmer Drought Index values were strongly negatively related to E280 ($r^2 = 0.38$–0.92) and the humification index ($r^2 = 0.07$–0.67). This suggests some climatic control of DOM character, with more aromatic compounds being exported during periods of wet soil conditions. Similar patterns have been observed for agricultural watersheds in the Midwestern United States, where more aromatic material is typically exported during high flow, but where tile drainage is a prominent feature of the landscape[7,29,30]. As such, DOM character may relate more strongly to shorter-term moisture conditions where rapid or artificial drainage is present[7,29,30] and to longer-term moisture in more naturally drained watersheds (this study). Given the broad scope of our study, we did not explicitly sample during short-term storm events, which may be an important cause of variable DOM character[7,29]. Nonetheless, the export of more aromatic DOM with increasing moisture conditions seems to be a consistent trend across regions.

Conversely, indicators of DOM source (fluorescence index and β/α) showed relatively consistent patterns between each of the 9 sampling dates ($r^2 = 0.27$–0.65 for fluorescence index and continuous cropland, $r^2 = 0.28$–0.76 for β/α and TDN) and no relationship to moisture conditions. Therefore, it seems probable that during changing climatic conditions, DOM retains some

Table 2 | Current and historic average DOC export over the nine-month ice-free season and fluorescence index for selected watersheds.

	Continuous cropland (%)	Wetland (%)	Area (km^2)	Current estimated 9 month DOC export (tons)	Historic 9 month DOC export (tons)	Current fluorescence index	Historic fluorescence index
Beaver River	18.2	19.1	291	370	682	1.28	1.23
Upper Nottawasaga River	22.2	11.3	218	195	378	1.30	1.25
Scugog River	18.0	17.5	993	1,560	1,970	1.27	1.24
Grand River*	29.6	7.7	3,008	3,240	6,870	1.32	1.22
Lake Erie* (only Canadian watersheds)	40.5	3.9	10,069	8,380	15,800	1.35	1.24
Lake Ontario* (Canadian watersheds south of the shield)	14.4	25.5	8,036	8,600	13,300	1.29	1.24

Historic export and fluorescence index are modelled based on the empirical relationships with watershed area and wetland coverage shown in Table 1. All current values were measured except for watersheds denoted with an asterisk, which were modelled.

structural characteristics (for example, chromophores) defined by source that are less susceptible to adsorption in the soil or photodegradation in the water (fluorescence index, β/α (ref. 15)), whereas other characteristics reflecting aromaticity (E280) are strongly affected. To test the regional consistency of this shift to more microbially derived DOM with agriculture, we obtained water samples on two sampling dates for ten streams located outside our initial study area and within the watersheds of lakes Erie and Huron (see Supplementary Information, Fig. S2). Indeed, we consistently find more autochthonous-like DOM with continuous cropland when we include sites outside our survey area ($r^2 = 0.63$ for fluorescence index, Supplementary Information, Fig. S3). Unlike continuous cropping, rotational cropping (rotation between perennial and annual crops) and rural land use (permanent perennial crops) were not correlated with DOM character within our initial study area or regionally. As such, it seems that continuous cropping, a more intense form of agriculture, is a more significant predictor of nutrient export and DOM character.

Unlike DOM character, organic carbon concentration (measured in units of dissolved organic carbon; DOC) is less related to agricultural land use[8]. When averaged over the two years of sampling, the percentage of poorly drained soils within the watershed and the proportion of wooded landcover were the most consistent predictors of DOC (Table 1). Wetland coverage was not a strong predictor of monthly or average DOC, but it was the only significant predictor, other than watershed area, that related to DOC export during the ice-free season (Table 1). Lower DOC exports are not uncommon in areas where forests have been lost at the expense of agriculture[6]. Given the multi-faceted role of wetlands as a carbon source, for DOM lability and in hydrological processes, this relationship between DOC export and wetlands is not surprising.

Where wetlands have been lost to continuous cropping, it can be expected that DOM will be metabolized at faster rates owing to increased microbial activity with nutrient loading[10]. It is less clear what effects this differential DOM character will have on overall stream metabolism. More simple DOM compounds[12,13] have often been associated with increased bioavailability and production. However, higher-molecular-weight DOM has also been identified as more degradable[14]. Clearly, future research needs to address the effects of the different types of DOM on microbial activity. Even if refractory-like DOM still comprises most of the carbon exported in agricultural systems, higher ambient nitrogen concentrations might be expected to disproportionately increase respiration. This increased availability could result in terrestrial DOM moving shorter distances before either being respired or incorporated within stream organisms or sediments. At broader scales, this trend could result in a reduction in the overall amount of DOM reaching downstream systems. The potential significance of these trends can be approximated using conservative estimates of wetland loss, modelled changes in export and associated changes in DOM character (Table 2). Our calculations show that along with a shift in more microbially derived DOM character, reductions in DOC export during the ice-free season of up to 50% may have occurred with land use conversion (Table 2). Our results also show that a shift in DOM character can be expected in regions where climate change is expected to modify precipitation rates, because indicators of DOM aromaticity strongly relate to moisture conditions. Given the importance of DOM in the global carbon cycle, the effects of agricultural land use and climate change on DOM chemical composition should be considered in predicting the dynamics of its transport through aquatic ecosystems.

Methods

Thirty-four moderately large watersheds were chosen from across south-central Ontario to represent a gradient in agricultural land use from within the same physicographic and hydrogeologic unit. The study watersheds fall within the larger Georgian Bay, Lake Simcoe and Otonabee River watersheds and historically were covered mainly by mixed forest (site details listed in Supplementary Information, Table S1, Fig. S2). Watersheds were characterized using geospatial data and historical landcover was estimated as described in Supplementary Information, Methods. Mean Palmers Drought Severity Index values were calculated for our study region using data from six regional climate stations (see Supplementary Information, Methods). Field sampling occurred either monthly or bi-monthly during the ice-free season of 2006 and 2007. Water samples were filtered through glass-fibre filters and membrane filters (pore size 0.22 μm) before DOM analysis and characterization. DOC and TDN were processed by combustion using an O.I. Analytical Aurora Model 1030 total organic carbon analyser with an external total bound nitrogen module. Discharge measurements were made in the field or obtained from the nearest Water Survey of Canada metering station. Calculations of monthly export were made by extrapolating daily discharge and DOC measurements across the number of days in each month. Average DOC export is estimated for a 9-month ice-free period by summing average monthly values. Absorbance was measured using a Perkin Elmer Lambda ultraviolet/visible scanning spectrophotometer. A blank of Milli-Q water was used as a reference for absorbance measurements. Spectrofluorometric 3D EEM measurements were made using a Varian Cary Eclipse fluorescence spectrophotometer. Fluorescence intensity measurements were made for excitation wavelengths from 250 to 450 nm at 1 nm increments and at emission wavelengths from 300 to 600 nm at 5 nm increments. All 3D EEM matrices were corrected for inner-filter effects using absorbance measurements and a Milli-Q blank was subtracted to remove most of the effects associated with Raman scatter[7]. β/α was calculated on the 310 nm excitation band because neither the β nor α component peaks were clearly defined, but were both present in this region of the EEM (Fig. 2 and Supplementary Information, Fig. S1). The β/α index was calculated as the ratio of emission intensity at 380 nm (β) to the maximum emission intensity observed between 420 and 435 nm (α) for an excitation wavelength of 310 nm. The fluorescence index was calculated as the ratio of emission intensity at 450 nm to that at 500 nm for an excitation wavelength of 370 nm (ref. 15). The interpretation of the fluorescence index can vary slightly depending on the machine used in its measurement. Representative values for microbial and terrestrial DOM are given in Supplementary Information, Methods. The humification index was measured using the excitation wavelength 254 nm and calculated as the ratio of the area under the emission spectra at 435–480 nm divided by the area under the 300–445 nm region[17]. Before analysis, both landscape and water chemistry variables were checked for normality and, when needed, were either log or square-root transformed. We used univariate regression analyses to test for the relationship between monthly and mean measurements of DOM character and landcover variables. Stepwise multiple regression analysis was used to detect relationships between average (over nine sampling dates) fluorescence index, E280, humification index, β/α values, landcover and water chemistry.

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Author contributions

H.F.W. and M.A.X. equally contributed to the conceptual and methodological development of the project. H.F.W. collected, processed and analysed the data and wrote the first draft. M.A.X. coordinated the study, contributed to the writing and edited the drafts.

Additional information

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