

# Long-term watershed management is an effective strategy to reduce organic matter export and disinfection by-product precursors in source water

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The authors wish to advise the original Fig. 6 was incorrectly labelled. The correct figure is provided below. All data provided in the text and tables in the paper is correct.

Watershed	Forest floor	Surface water quality	DBPs
Managed (Watershed 77)	12.3 ± 1.1 Mg ha <sup>-1</sup> Litter mass	21.94 ± 1.8 DOC (mg L <sup>-1</sup> )	2143 ± 136 THM-FP (µg L <sup>-1</sup> )
	5.8 ± 1.6 Mg ha <sup>-1</sup> Duff mass	0.9 ± 0.08 TDN (mg L <sup>-1</sup> )	43.0 ± 4.2 HAN-FP (µg L <sup>-1</sup> )
Unmanaged (Watershed 80)	12.5 ± 0.7 Mg ha <sup>-1</sup> Litter mass	24.95 ± 2.6 DOC (mg L <sup>-1</sup> )	2667 ± 192 THM-FP (µg L <sup>-1</sup> )
	10.5 ± 1.4 Mg ha <sup>-1</sup> Duff mass	1.0 ± 0.1 TDN (mg L <sup>-1</sup> )	66.5 ± 6.0 HAN-FP (µg L <sup>-1</sup> )

**Fig. 6.** Long-term forest management may alter long-term detrital mass and chemistry in favour of improved water quality by reducing dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentration, and thus, disinfection by-products (DBPs) formation potential (FP). The values (mean ± standard deviation) represent the results from the field study. HAN, haloacetonitrile; THM, trihalomethane.

# Long-term watershed management is an effective strategy to reduce organic matter export and disinfection by-product precursors in source water

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**Abstract.** Watershed management practices such as prescribed fire, harvesting and understory mastication can alter the chemical composition and thickness of forest detritus, thus affecting the quantity and quality of riverine dissolved organic matter (DOM). Long-term effects of watershed management on DOM composition were examined through parallel field and extraction-based laboratory studies. The laboratory study was conducted using detritus samples collected from a pair of managed and unmanaged watersheds in South Carolina, USA. Results showed that dissolved organic carbon (DOC), total dissolved nitrogen (TDN) and ammonium ( $\text{NH}_4^+\text{-N}$ ) concentrations were higher in water extracts from the unmanaged watershed than from the managed watershed ( $P < 0.01$ ). Pyrolysis gas chromatography–mass spectrometry analysis showed that water extracts from the unmanaged watershed contained more aromatic compounds than extracts from the managed watershed. For the field study, monthly water samples were collected for 1 year (2015) from the paired watersheds. DOC and TDN concentrations, as well as DOM aromaticity, were significantly higher in the unmanaged watershed than in the managed watershed for most of the year ( $P < 0.05$ ) and were linked to detrital thickness, precipitation and flow patterns. The formation potential of two regulated disinfection by-products was lower in the unmanaged watershed for most of 2015 ( $P < 0.05$ ). From this study, it appears that long-term watershed management practices may alter detrital mass and chemistry in ways that improve water quality.

**Additional keywords:** carbon, forest management, fuels, harvesting, mastication, prescribed fire, water quality.

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## Introduction

Prescribed fire, harvesting and understory mastication are common forest management practices (Van Lear *et al.* 2005)

that might enhance forest health and wildlife habitat by reducing wildfire hazard and controlling invasive and undesired vegetative species (Stanturf *et al.* 2002; Block and Conner 2016;

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Waldrop *et al.* 2016). In addition, the depth and composition of forest detritus (defined as both litter and various degrees of decomposing litter and debris, also known as duff) might be altered by management practices. The absence of management practices for retention of slash or coarse woody debris following disturbances, such as hurricanes, can also affect the quantity, composition and dynamics of carbon and organic matter (McNulty 2002). Such disturbances release nutrients that can increase short-term forest productivity while reducing stand density and, potentially, soil carbon storage (McNulty 2002). Thus, active management practices (or the lack thereof) can potentially alter the depth and composition, organic matter content and dynamics of forest detritus and subsequently forest vegetation (Bettinger *et al.* 2017).

The quality of both source water and drinking water can be affected by alterations in detrital depth and composition because these properties have shown linkages to the concentration and composition of riverine dissolved organic matter (DOM) (Chow *et al.* 2009; Majidzadeh *et al.* 2015; Chen *et al.* 2019). Riverine DOM has not only been linked to ecosystem function and global carbon cycling, but has also been associated with concerns regarding drinking water constituents through the formation of regulated and unregulated disinfection by-products (DBPs) (Seitzinger *et al.* 2002; Inamdar *et al.* 2011; Linkhorst *et al.* 2017; Majidzadeh *et al.* 2017). Regulated DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), and some unregulated DBPs, such as nitrogenous DBPs (i.e. haloacetonitriles (HANs)), have exhibited carcinogenic properties. Exposure to these compounds might adversely affect human health, including increased occurrence of bladder cancer, rectal cancer and adverse birth outcomes (Plewa *et al.* 2002; Zeng *et al.* 2016). Therefore, the USA Environmental Protection Agency's Stage 2 disinfectants and DBPs rule enforces maximum drinking water contamination concentration limits of  $80 \mu\text{g L}^{-1}$  for THMs and  $60 \mu\text{g L}^{-1}$  for HAAs (Richardson *et al.* 2007).

Under the appropriate conditions, forest management practices such as prescribed fire and forest harvesting might reduce excessive fuel loads and reduce stand density (Van Lear *et al.* 2005; Waldrop and Goodrick 2012). In contrast to severe wildfires, most prescribed fires, particularly in the southeastern USA, are implemented under specific constraints of fuel characteristics, fire frequency and weather to be both low intensity and low severity (Keeley 2009). These conditions minimise forest floor consumption, mineral soil exposure and subsequent erosion (Stanturf *et al.* 2014; Holland *et al.* 2017). Likewise, most harvesting operations exercised in the USA comply with recommended best management practices (BMPs) and induce little long-term detrimental effects to forested watersheds (Fulton and West 2002). Potential harvesting effects are influenced by the extent of material removed from a site and the extent at which harvesting machinery negatively affects soil bulk density and surface soil physical properties, such as detrital mass and depth (Johnson and Curtis 2001). Nave *et al.* (2010) in a global meta-analysis also stated that species composition, soil taxonomic order and time since harvest influenced carbon-related harvesting effects. Therefore, water quality appears to be minimally affected as a direct result of low-intensity, low-severity prescribed surface fires

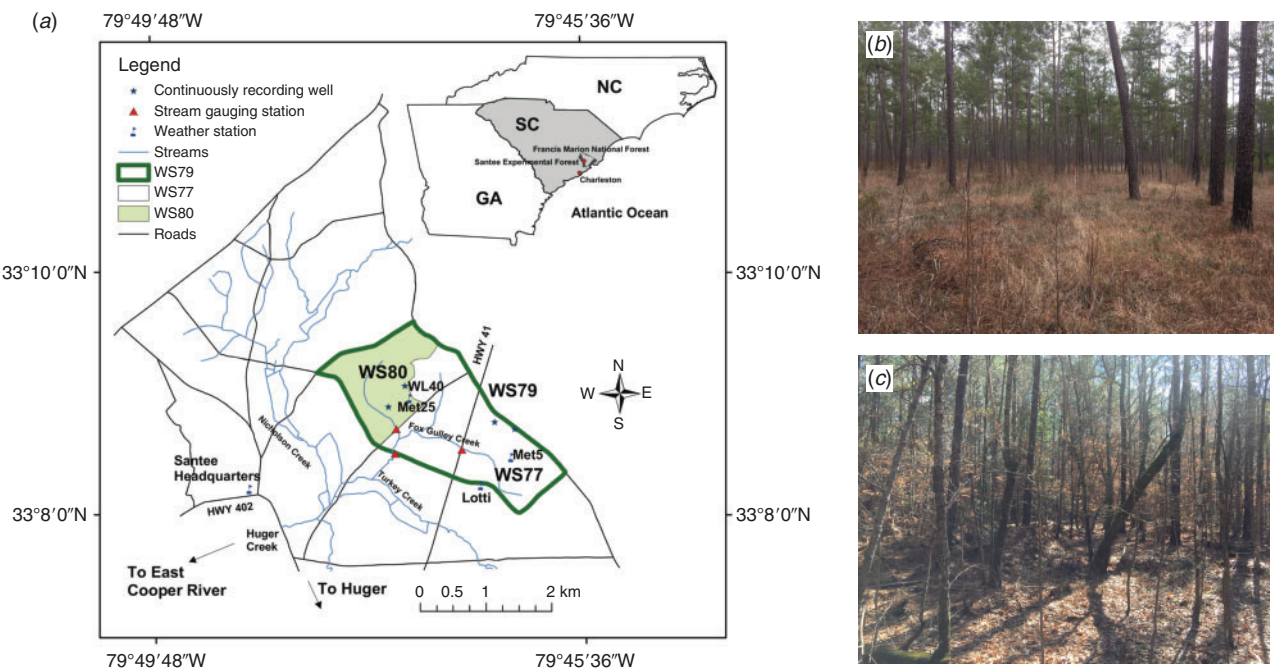
and harvesting practices that comply with recommended BMPs (Fulton and West 2002; Waldrop and Goodrick 2012). However, both the short- and long-term effects of wildland fire and forest management practices on detrital layer composition and water quality are unclear. Moreover, management practices such as salvage logging after natural disturbances such as hurricanes or windstorms can also affect detrital layer composition and thickness and soil chemistry (McNulty 2002; Foster and Orwig 2006; Fernández *et al.* 2007). Hurricanes and storm events can significantly increase the down and dead biomass on the forest floor, which in turn can alter soil chemistry (McNulty 2002) and the export of nutrients and organic matter during storm events (Jayakaran *et al.* 2014; Majidzadeh *et al.* 2017; Chen *et al.* 2019).

Although the immediate effects of forest management practices such as prescribed fire on water quality have been studied (Majidzadeh *et al.* 2015; Tsai *et al.* 2015; Wang *et al.* 2015), there is a paucity of information concerning the long-term effects of watershed management on forest detritus and water quality, especially regarding the formation of DBPs. To investigate this issue, we conducted parallel laboratory and field studies on a pair of watersheds (managed and unmanaged) in coastal South Carolina, USA. The unmanaged watershed has not been subjected to active forest management since 1968 and remains in its natural unmanaged condition (i.e. unaffected by any nearby wildland fires). However, during this same period, the managed watershed was affected by salvage harvesting (following a major hurricane), thinning, understory mastication and prescribed fire. Most recently, since 2003 this forest has been burned every 2–4 years. Litter and duff samples were collected for an extraction-based laboratory study to examine long-term watershed management effects on DOM composition. In addition, monthly water samples were collected for 1 year at both watersheds and characterised for DOM quantity, quality and the formation of carbonaceous and nitrogenous DBPs.

## Materials and methods

### Study site

Two experimental, coastal, first-order watersheds within the Santee Experimental Forest of the Francis Marion National Forest in Cordesville, South Carolina, USA were utilised for this study (Fig. 1). Land comprising this forest has been used for agriculture and forestry since the early 1700s (Amatya *et al.* 2007). The unmanaged watershed, Watershed 80, is a 160-ha watershed that has not been subjected to active forest management since 1968 and serves as a control site for the USDA Forest Service Southern Research Station Center for Forested Wetlands Research (Amatya and Trettin 2007). The managed watershed, Watershed 77, is a 160-ha watershed that has been actively managed by many silvicultural practices since 1963 (Table 1). One large natural disturbance of note affecting both watersheds in 1989 was Hurricane Hugo; ~80% of the dominant trees in the area were broken or uprooted (Hook *et al.* 1991). None of the post-hurricane debris was removed from the unmanaged watershed and no silvicultural practices were utilised for stand recovery. The managed watershed was salvage-harvested in 1990 (Amatya *et al.* 2007). Since 2003, the



**Fig. 1.** Location of the (a) study site and images from sites at the (b) managed (Watershed 77) and (c) unmanaged (Watershed 80) watersheds at Santee Experimental Forest, Francis Marion National Forest, Cordesville, South Carolina (SC), USA (Harder et al. 2006). Water samples were collected from hydrometric gauging stations (shown with red circles). GA, Georgia; NC, North Carolina.

**Table 1.** Chronology of forest management activities or natural disturbances occurring on both the managed (Watershed 77) and unmanaged watershed (Watershed 80) of the United States Department of Agriculture (USDA) Forest Service, Francis Marion National Forest, Cordesville, South Carolina, USA

Year	Description of treatment or disturbance
1963	Watershed 77 established as a managed treatment watershed
1968	Watershed 80 established as a control (unmanaged) watershed
1977–1981	100% of Watershed 77 prescribed burned at various times over 5-year period
1989	Hurricane Hugo damages 80% of forest (September)
1990	Watershed 77 is salvage-harvested (entire vegetation harvested and removed); Watershed 80 is left untouched
2001	Mastication of understory vegetation occurred on Watershed 77 (February–November)
2003	Watershed 77 prescribed burned on 10 May
2006	Watershed 77 whole-tree thinning of understory in early July
2007	Watershed 77 prescribed burned on 7 June
2009	Watershed 77 prescribed burned on 21 April
2013	Watershed 77 prescribed burned on 5 March

managed watershed has been burned every 2–4 years (Table 1). Additionally, understory vegetation was masticated in 2001 and a whole-tree understory thinning was conducted in 2006. The dominant tree species on both watersheds are loblolly pine (*Pinus taeda*), sweetgum (*Liquidambar styraciflua*) and oaks (*Quercus* spp.). According to Coates (2017), mean total basal area

at the time of our study was greater in the unmanaged watershed ( $46.35\text{ m}^2\text{ ha}^{-1}$ ) than in the managed watershed ( $33.72\text{ m}^2\text{ ha}^{-1}$ ,  $P = 0.02$ ). Further analyses based on broad species categories suggested that mean softwood (predominantly *Pinus* spp.) basal area was greater on the managed watershed ( $27.1\text{ m}^2\text{ ha}^{-1}$ ) than on the unmanaged watershed ( $19.0\text{ m}^2\text{ ha}^{-1}$ ) ( $P = 0.02$ ) and mean hardwood basal area was greater on the unmanaged watershed ( $26.6\text{ m}^2\text{ ha}^{-1}$ ) than on the managed watershed ( $7.4\text{ m}^2\text{ ha}^{-1}$ ) ( $P < 0.001$ ). Pines accounted for 81% of the basal area in the managed watershed and 41% of the basal area in the unmanaged watershed. The soils have developed in the riparian zones to moderately well drained in the uplands. They are defined as aquic Alfisols or Ultisols, containing argillic horizons (Jayakaran et al. 2014). Both managed and unmanaged watersheds are responsive to rainfall events and stream outflows can receive up to 46% of the rainfall. However, higher discharge rates are often observed in the managed watershed, probably because of reduced evapotranspiration rates (Amatya et al. 2007).

Water and detrital sampling

To obtain the detrital samples, a randomised sampling grid was established in each watershed: 20 locations were established ~300 m apart. During January–February 2015, three  $0.30 \times 0.30\text{ m}$  (1 ft  $\times$  1 ft) destructive samples of forest detritus were taken ~1 m apart at each location. Litter and duff depth were obtained for each sample. Each sample was taken back to the laboratory and oven-dried at  $65^\circ\text{C}$  for not less than 48 h to obtain an oven-dry mass. These samples were then ground using a Wiley mill (2-mm sieve).



Litter and duff samples collected from each watershed were also used for a laboratory extraction study. Four treatments (litter<sub>managed</sub>, litter<sub>unmanaged</sub>, duff<sub>managed</sub> and duff<sub>unmanaged</sub>) were prepared by mixing 2 g of litter or duff samples with 200 mL of Milli-Q water in a 250-mL Erlenmeyer flask for 1 h. Each treatment was replicated three times. In addition to the laboratory study, monthly water samples were collected at the outflow of both the managed and unmanaged watersheds for 1 year (January–December 2015). Water samples were collected with 1-L precleaned amber bottles to determine water quality and DBP formation potential (FP).

### Analytical methods

All water samples were filtered through a prewashed 0.45- $\mu\text{m}$  membrane filter before analysis. Shimadzu TOC-VcPN (Shimadzu Corporation, Kyoto, Japan) and Shimadzu TNM-1 analysers were used to quantify DOC and total dissolved nitrogen (TDN). Ultraviolet (UV) absorbance was measured using a Shimadzu UV-1800 at room temperature in a 1-cm quartz cell. UV absorbance at 254 nm was normalised to the DOC concentration to calculate the specific UV absorbance at 254 nm (SUVA<sub>254</sub>), which has been shown to directly correlate with DOM aromaticity. Three-dimensional (3D) spectrofluorometry (Shimadzu Spectrofluorometer RF5301) was used for more detailed optical measurements to quantify the humification index (HIX) and freshness index (FI). The HIX positively correlates with the abundance of humic substances (Fellman *et al.* 2009) and was calculated by dividing the area under emission spectra 435–480 nm by the sum of peak areas at 300–345 nm and 435–480 nm, at Ex 254 nm (Ohno 2002). The FI indicates microbial ( $\sim 1.8$ ) or terrestrial origins of DOM ( $\sim 1.2$ ).

The FP of commonly formed carbonaceous and nitrogenous DBPs was quantified using chlorine as a disinfectant. Four THMs (trichloromethane, dichlorobromomethane, dibromochloromethane, and tribromomethane) and four HANs (trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile) were quantified. Samples were diluted to a DOC concentration of  $\sim 3 \text{ mg L}^{-1}$ , buffered by an  $\text{H}_3\text{BO}_3/\text{NaOH}$  solution to pH 8.0, and chlorinated with freshly prepared  $\text{NaOCl}/\text{H}_3\text{BO}_3$  solution (pH 8.0) at 25°C in the dark for 24 h without headspace. After reaction, the residual chlorine was quenched by 10%  $\text{Na}_2\text{SO}_3$  solution, and DBPs were extracted using 3 mL of methyl-*t*-butyl ether and quantified by gas chromatography with electron capture detector (Agilent 7890, Agilent Technologies Inc., Santa Clara, CA, USA). 1,2-dichlorobenzene was used as the internal standard.

It should be noted that particulate organic matter, including particulate black carbon, might have a significant effect on the quality of both source and drinking water (Dhillon and Inamdar 2013; Liu *et al.* 2017). However, it was not measured as part of this study and goes beyond the scope of our results and discussion.

### Pyrolysis gas chromatography–mass spectrometry (pyrolysis GC/MS)

The water extracts were iced overnight at  $-20^\circ\text{C}$  and then freeze-dried at  $-80^\circ\text{C}$  (FreeZone 1 Liter Benchtop, Labconco, MO, USA). A quartz tube (for 0.64 cm probes, CDS Analytical Inc., Oxford, PA, USA) was filled with quartz wool (CDS Analytical

Inc.) at the bottom, loaded with 3–9 mg of solid samples (depending on the organic carbon content) and then covered with quartz wool. Both the quartz tube and wool were pre-treated at  $1100^\circ\text{C}$  for 10 s using a CDS 5000 pyro-probe (CDS Analytical Inc.). Once the sample was loaded, the quartz tube was inserted again into the pyrolysis probe, heated from  $250^\circ\text{C}$  to  $700^\circ\text{C}$  at a rate of  $5^\circ\text{C ms}^{-1}$  and held for 10 s. The pyrolytic products were transferred to an Agilent GC7980 gas chromatograph combined with a 220-ion trap mass spectrometer (Agilent) using helium as the carrier gas at  $1 \text{ mL min}^{-1}$ . The GC column (DB-5MS,  $30 \times 0.32 \text{ mm ID}$ ,  $0.25 \mu\text{m}$  film thickness, J&W Scientific Inc., Folsom, CA, USA) was maintained at  $35^\circ\text{C}$  for 5 min, increased to  $300^\circ\text{C}$  at a rate of  $3^\circ\text{C min}^{-1}$  and held at  $300^\circ\text{C}$  for 10 min. Signal recording by the mass spectrometer began after 2 min using a mass detection range of  $m/z$  50–550 and an electron ionisation of 70 eV. Extracting pyrolysate information for the leachates from the pyrolysis GC/MS data was based on an automated pipeline method developed by Chen *et al.* (2018). Specifically, eight chemical classes, comprising lignin compounds (LgC), phenol compounds (PhC), carbohydrates (Carb), saturated hydrocarbons (SaH), unsaturated hydrocarbons (UnSaH), nitrogen-containing compounds (Ntg), aromatic hydrocarbons (ArH), and polyaromatic hydrocarbons (PAH), were used to classify the pyrolytic products (see Tables S1, S2 in Supplementary Material available online).

### Data analysis

We used RStudio Desktop version 1.0.44 (Boston, MA, USA) for statistical analyses and data visualisation. Factor analysis was conducted with the *fa* functions in the *psych* package to highlight the variability in pyrolysis products among samples. Time-series analyses were conducted to evaluate changes in water quality over time using a linear model (*P*-value and standard deviation are reported). Tukey's honestly significant difference (HSD) following an analysis of variance test was used (*Agricola* package,  $\alpha = 0.05$ ) to differentiate the means of DOC, TDN, DOM optical properties and DBPs FP in the laboratory extraction studies in which the four treatments (litter<sub>managed</sub>, litter<sub>unmanaged</sub>, duff<sub>managed</sub> and duff<sub>unmanaged</sub>) were replicated three times.

## Results and discussion

### Forest management reduces export of DOM

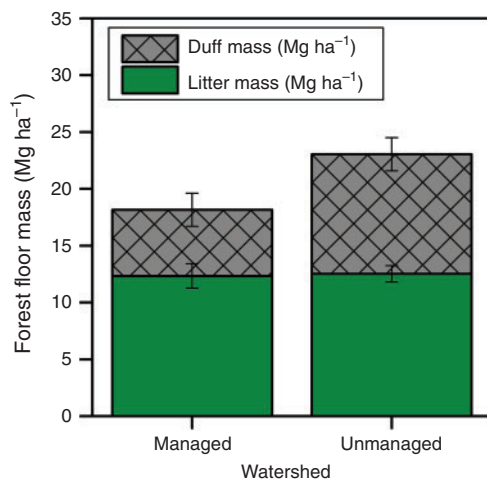
#### Laboratory water extraction study

Litter and duff samples were collected from both the managed and unmanaged watersheds approximately 2 years after the last prescribed fire for an extraction-based laboratory study to examine long-term effects of watershed management on DOM composition. The characteristics of the water extracts were compared between the managed and unmanaged watersheds using four treatments: litter<sub>managed</sub>, litter<sub>unmanaged</sub>, duff<sub>managed</sub> and duff<sub>unmanaged</sub> (Table 2). Litter DOC concentration was similar between the two watersheds (litter<sub>managed</sub> = litter<sub>unmanaged</sub>,  $P = 0.3$ ). However, duff DOC concentration was  $1.7 \text{ mg g}^{-1}$  litter ( $\pm 0.4$ ,  $P = 0.04$ ) higher at the unmanaged watershed compared with the managed watershed (duff<sub>managed</sub> > duff<sub>unmanaged</sub>, Table 2). This difference in DOC concentration was based on the extraction study in which we used the same

**Table 2.** Characteristics of water extracts from litter and duff layers collected from the managed (WS77) and unmanaged (WS80) watersheds ( $n = 5/\text{treatment}$ )

Means are significantly different with different letters based on Tukey's honest significant difference tests at  $\alpha = 0.05$ . DOC, dissolved organic carbon; FI, freshness index; FP, formation potential; HAN, haloacetonitriles; HIX, humification index;  $\text{NO}_3^- \text{N}$ , nitrate; SHAN FP, specific HAN FP; STHM FP, specific THM FP;  $\text{SUVA}_{254}$ , specific UV absorbance; TDN, total dissolved nitrogen; THM, trihalomethanes

Parameter	Managed watershed (WS77)		Unmanaged watershed (WS80)	
	Leaf litter	Duff	Leaf litter	Duff
DOC ( $\text{mg g}^{-1}$ detritus)	$14.0 \pm 0.40^a$	$6.4 \pm 0.90^c$	$14.4 \pm 2.40^a$	$8.1 \pm 0.90^b$
TDN ( $\text{mg g}^{-1}$ detritus)	$0.18 \pm 0.02^c$	$0.15 \pm 0.04^d$	$0.25 \pm 0.09^a$	$0.21 \pm 0.04^b$
DOC-export ( $\text{kg ha}^{-1}$ )	$175.4 \pm 5.10^a$	$85.1 \pm 8.41^b$	$177.7 \pm 29.60^a$	$37.3 \pm 4.08^c$
TDN-export ( $\text{kg ha}^{-1}$ )	$3.1 \pm 1.10^a$	$0.87 \pm 0.20^c$	$2.2 \pm 0.20^b$	$2.21 \pm 0.40^b$
$\text{NH}_4^+ \text{-N}$ ( $\text{mg g}^{-1}$ detritus)	$0.07 \pm 0.04^c$	$0.06 \pm 0.02^c$	$0.10 \pm 0.03^b$	$0.14 \pm 0.04^a$
$\text{NO}_3^- \text{N}$ ( $\text{mg g}^{-1}$ detritus)	$0.01 \pm 0.00^a$	$0.01 \pm 0.00^a$	$0.01 \pm 0.00^a$	$0.01 \pm 0.00^a$
$\text{SUVA}_{254}$ ( $\text{L mg C}^{-1} \text{m}^{-1}$ )	$8.5 \pm 0.90^a$	$10.7 \pm 1.00^a$	$8.5 \pm 1.60^a$	$9.0 \pm 2.70^a$
HIX	$1.10 \pm 0.31^a$	$0.88 \pm 0.20^a$	$1.37 \pm 0.36^a$	$1.06 \pm 0.30^a$
FI	$1.48 \pm 0.03^a$	$1.51 \pm 0.03^a$	$1.45 \pm 0.04^a$	$1.47 \pm 0.02^a$
THM FP ( $\mu\text{g L}^{-1}$ )	$5748 \pm 1162^a$	$2941 \pm 650^b$	$4710 \pm 426^a$	$3242 \pm 189^b$
STHM FP ( $\mu\text{g mg}^{-1}\text{-DOC}$ )	$40.9 \pm 7.6^a$	$42.8 \pm 9.1^a$	$34.7 \pm 3.1^a$	$42.7 \pm 5.5^a$
HAN FP ( $\mu\text{g L}^{-1}$ )	$926 \pm 103^{ab}$	$361 \pm 116^c$	$991 \pm 206^a$	$588 \pm 61^b$
SHAN FP ( $\mu\text{g mg}^{-1}\text{-DOC}$ )	$6.6 \pm 0.9^{ab}$	$6.3 \pm 0.7^b$	$7.2 \pm 0.4^a$	$7.4 \pm 1.4^a$



**Fig. 2.** Duff and litter mass in the managed (WS77) and unmanaged (WS80) watersheds ( $\text{Mg ha}^{-1}$ ) ( $n = 10$  per watershed). Duff mass was 44.3% higher for the unmanaged watershed than for the managed watershed ( $P < 0.001$ ).

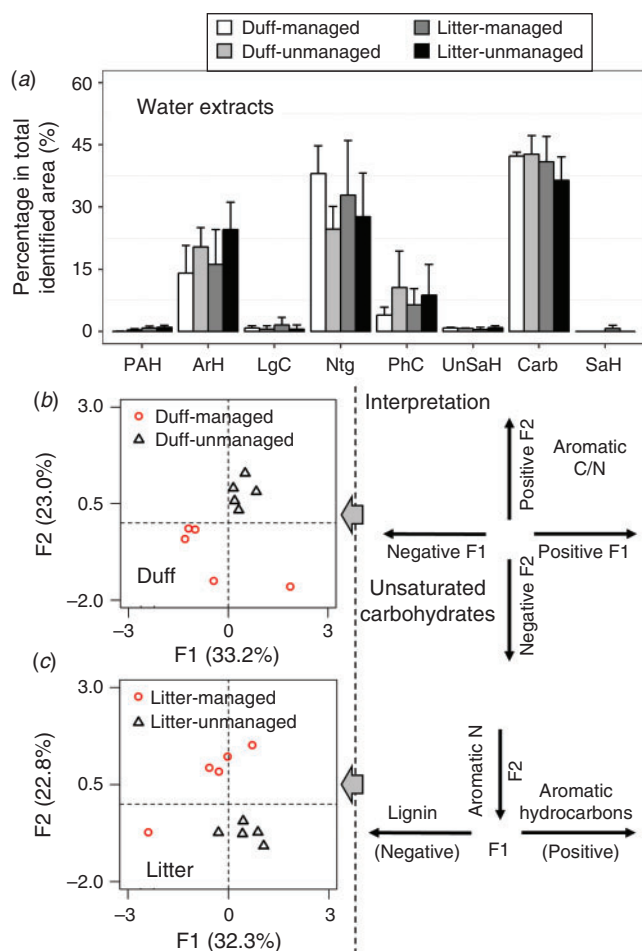
amount of litter and duff (2 g) for each treatment. As reported by Coates (2017), a lack of active management in the unmanaged watershed resulted in greater forest floor depth. In particular, duff mass was 44.3% higher at the unmanaged watershed than at the managed watershed ( $P < 0.001$ , Fig. 2); however, litter mass was similar between watersheds. Thus, to better understand the effects of watershed management on terrestrial DOM, the DOC and TDN values were normalised by duff mass. Normalised data suggested that potential duff layer DOC export would be significantly higher in the managed watershed ( $85.1 \pm 8.41 \text{ kg ha}^{-1}$ ) than in the unmanaged watershed ( $37.3 \pm 4.08 \text{ kg ha}^{-1}$ ,  $P < 0.001$ ), assuming that precipitation is not a limiting factor during storm events. However, potential litter DOC export was similar between watersheds ( $177.7 \pm 29.6$  and

$175.4 \pm 5.1 \text{ kg ha}^{-1}$  from the unmanaged and managed watersheds respectively, Table 2).

The TDN concentration was significantly higher at the unmanaged watershed than at the managed watershed ( $P = 0.03$ ) for both the litter and duff treatments (Table 2). Similar to DOC, the concentration values were normalised by detrital mass, which showed TDN export in the order of  $\text{litter}_{\text{managed}} (3.1 \pm 1.1 \text{ kg ha}^{-1}) > \text{litter}_{\text{unmanaged}} (2.2 \pm 0.2 \text{ kg ha}^{-1}) = \text{duff}_{\text{unmanaged}} (2.21 \pm 0.4 \text{ kg ha}^{-1}) > \text{duff}_{\text{managed}} (0.87 \pm 0.2 \text{ kg ha}^{-1})$ . Ammonium ( $\text{NH}_4^+ \text{-N}$ ) also followed a similar pattern to TDN, with higher water extract concentrations from the unmanaged watershed than from the managed watershed. However, although the highest concentrations of extractable  $\text{NH}_4^+ \text{-N}$  were observed for the  $\text{duff}_{\text{unmanaged}}$  treatment, the lowest concentration of extractable  $\text{NH}_4^+ \text{-N}$  was observed for  $\text{duff}_{\text{managed}}$ , revealing a significant difference between the duff layers in the managed and unmanaged watersheds. This may be the result of natural humification in the unmanaged watershed in the absence of any human-induced disturbances, including fire-related volatilisation losses.

Optical properties of the water extracts were also measured to quantify DOM aromaticity (i.e.  $\text{SUVA}_{254}$ ), abundance of humic substances (i.e. HIX) and the FI, the latter used to indicate microbial ( $\sim 1.8$ ) or terrestrial ( $\sim 1.2$ ) origins of the DOM. No statistical differences were observed between the optical properties of water extracts from the two watersheds. However, the  $\text{duff}_{\text{managed}}$  treatment, although not statistically significant ( $P = 0.1$ ), had the lowest HIX and the highest aromaticity. This may be attributed to the volatilisation of humic substances associated with periodic prescribed fire.

Chemical classes in the litter and duff water extracts were also identified using pyrolysis GC/MS. Overall, the water extracts from all treatments were dominated by Carb, Ntg and ArH, accounting for 73.3–95.9% of the total quantified peak area. This may be related to the solubility of these compounds (Fig. 3a). LgC and PhC are exclusively related to plant material and are not



**Fig. 3.** (a) Percentage (mean  $\pm$  standard deviation) of chemical classes in water extracts. Factor analysis on the relative percentage of pyrolysates from the water extracts of duff (b) and litter (c) samples at the managed and unmanaged watersheds. The loadings from factor analysis are presented in Figs S1 and S2 in the Supplementary Material. ArH, aromatic hydrocarbons; C/N, carbon/nitrogen; Carb, carbohydrates; LgC, lignin compounds; Ntg, nitrogen-containing compounds; PAH, polyaromatic hydrocarbons; PhC, phenol compounds; SaH, saturated hydrocarbons; UnSaH, unsaturated hydrocarbons.

water-soluble (Schellekens *et al.* 2017). UnSaH and Carb could originate from plant-derived and/or microbial polysaccharides (Weiss and Kaal 2018), which display a wide range of water solubility from insoluble (e.g. cellulose) to hot water-soluble (e.g. starch) to cold water-soluble (e.g. pullulan) (Xu 2017). Ntg originate from plant protein and microbial materials (Buurman *et al.* 2007), which also present a wide range of water solubility. Various compounds, including LgC, polysaccharides, and proteins, can be sources of ArH and PAH (Schellekens *et al.* 2017).

The factorial analysis revealed that water extracts from the duff<sub>unmanaged</sub> treatment contained more aromatic carbon and nitrogen, whereas the duff<sub>managed</sub> extracts contained more UnSaH (Fig. 3b). Litter extract results suggested that the unmanaged watershed might export more aromatic nitrogen than the managed watershed (Fig. 3c). More information on the interpretation of factor analysis is detailed in Fig. S1 and S2 in

the Supplementary Material. Overall, although the optical properties such as SUVA, excitation-emission matrix and HIX did not show any difference in either the litter or duff extractable organic matter chemical composition related to forest management practices (Table 2), the pyrolysis GC/MS results revealed that the organic matter leaching from the litter and duff layers of the unmanaged watershed contained more aromatic carbon and nitrogen compounds, respectively, compared with the managed watershed. The abundance of aromatic compounds in the unmanaged watershed extracts was not anticipated and might be the result of natural humification in the unmanaged watershed in the absence of any fire-related volatilisation losses, whereas the aromatic compounds formed during the prescribed fires in the managed watershed had lower water solubility because of loss of the -OH and/or -COOH groups (Wang *et al.* 2015). Accumulations of coarse woody debris resulting from Hurricane Hugo in the unmanaged watershed might be a causal factor in this result. Wade *et al.* (1993) recorded estimates of coarse woody debris on the adjacent, Hurricane Hugo-affected Francis Marion National Forest research plots ranging between 30.3 and 144.0 Mg ha<sup>-1</sup> in 1990. Although these estimates did not fully provide an approximation of the change in these amounts related to the hurricane, this event greatly increased the coarse woody debris loading that was not treated by any means on the unmanaged watershed. In comparing the mineral soils between the two watersheds in 2009, there was ~13% more carbon in the upper 30 cm of the unmanaged watershed as compared with the managed watershed and most of that difference was in the 0–10 cm soil layer.

Moreover, when interpreting these results, it must also be noted that forest composition differs between the managed and unmanaged watersheds (Coates 2017), including differences in mean basal area (unmanaged watershed > managed watershed), mean softwood basal area (managed watershed > unmanaged watershed) and mean hardwood basal area (unmanaged watershed > managed watershed). The presence of more hardwoods in the unmanaged watershed is related to the lack of active forest management since 1968. These watersheds were originally paired in part because of similar forest composition. Thin-barked species that are generally confined to bottomlands might increase in abundance across the landscape in the absence of fire and other disturbances (Waldrop and Goodrick 2012). Fire and thinning have maintained lower stocking levels in the managed watershed and have most likely influenced the reduction in hardwood species. Vegetation type can have significant effects on organic matter recalcitrance and also DOM quality. For example, Majidzadeh *et al.* (2015) showed that DOM aromaticity (i.e. SUVA<sub>254</sub>) leaching from pine litter was lower than from sweetgum litter, a deciduous, hardwood species. Other studies have also shown that leachate from coniferous and deciduous litter might have different DOM composition, including aromaticity and compositions of humic-like and protein-like molecules (Fox and Comerford 1990; Yamashita *et al.* 2011; Thieme *et al.* 2019).

#### Monthly field monitoring

In addition to the litter and duff extraction laboratory study, monthly water samples were collected from both watersheds for 1 year. The field study results suggested that DOC concentration



was significantly greater in the unmanaged watershed than in the managed watershed for most of 2015 (Fig. 4a,  $P < 0.05$ ), which agreed with the laboratory study results. However, from May through September, the DOC concentration was either greater in the managed watershed or not significantly different between the two watersheds, a result that might be attributed to water flow paths. Because of reduced precipitation during this period, water flow significantly decreased and was mainly limited to baseflow contributions. Baseflow contributions appeared to be higher in the managed watershed, as management practices can reduce evapotranspiration (Bosch and Hewlett 1982). However, in other months with contributions of surface flow, forest detritus might serve as the major source of organic matter (Chow *et al.* 2009). This might be observed by the presence of a thicker detrital layer at the unmanaged watershed and coincident higher DOC concentrations. TDN also followed the DOC pattern and was similarly linked to detrital thickness, precipitation and flow patterns (Fig. 4b).

In addition to changes in DOM quantity, we were also interested in quantifying changes in DOM quality and chemical composition. DOM aromaticity (i.e.  $SUVA_{254}$ ) was higher in the managed watershed in 8 of the 12 sampling months (Fig. 4c). This result might be related to (a) increased leaching of aromatic compounds from burned litter and duff or (b) higher contributions of subsurface flow in the managed watershed, which flushed aromatic OM from organic-rich soil horizons in the riparian zones into streams. The second assumption seems plausible because even during dry months of the year with no storm events and a sole contributor of subsurface flow,  $SUVA$  was higher at the unmanaged watershed. The laboratory extraction study confirmed this hypothesis as well; aromaticity of the DOM leaching from vegetation was not significant between the two watersheds (Table 2). This agrees with previous studies suggesting that low-intensity prescribed fire may not significantly change DOM composition and only high-intensity fire results in increased DOM aromaticity (Wang *et al.* 2015; Coates *et al.* 2017; Hahn *et al.* 2019).

#### Long-term forest management alters export of DBP precursors

Watershed management may alter DOM quantity and quality, as discussed here, thus affecting the formation of carcinogenic DBPs such as THMs and HAAs. The FP of THM and HAN was quantified using both water extracts (laboratory study) and samples collected monthly from the two watersheds to elucidate watershed management effects on drinking water quality.

In the monthly field samples, the THM FP patterns were similar to those for DOC and were higher at the unmanaged watershed than at the managed watershed, except for 4 months with low precipitation (May–August, Fig. 5), which can be attributed to a positive relationship between THM FP and DOC concentrations at both watersheds ( $P < 0.001$ ,  $r^2 = 0.82$ ). The positive relationship between THM FP and DOC concentration has been observed in other studies (Chow *et al.* 2011; Majidzadeh *et al.* 2015; Wang *et al.* 2015). Moreover, DOM reactivity to form THM (i.e. STHM FP), which was calculated by normalising THM FP by DOC concentration, was similar between the managed and unmanaged watersheds, further confirming the concept that THM FP was mostly

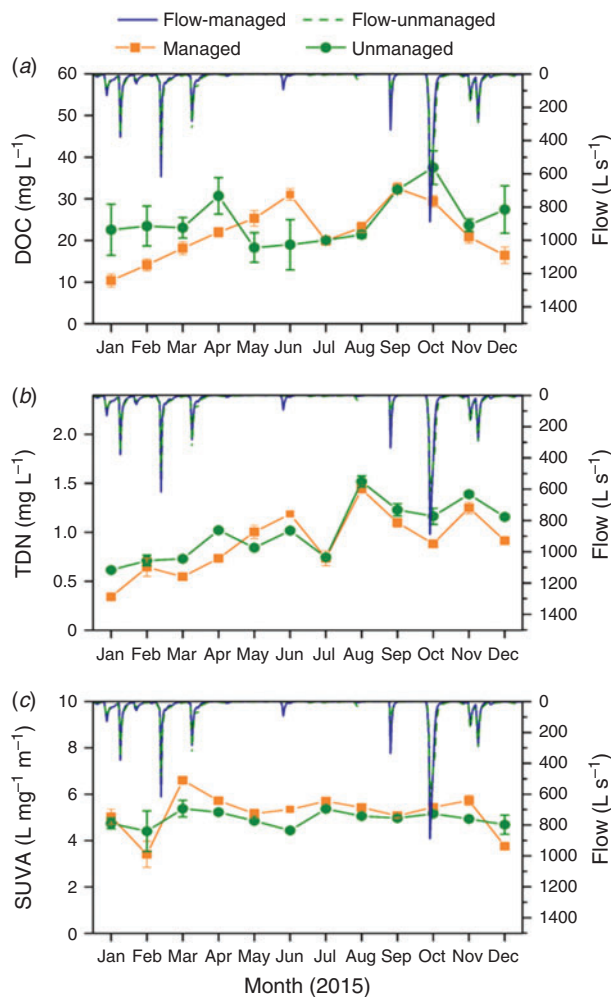


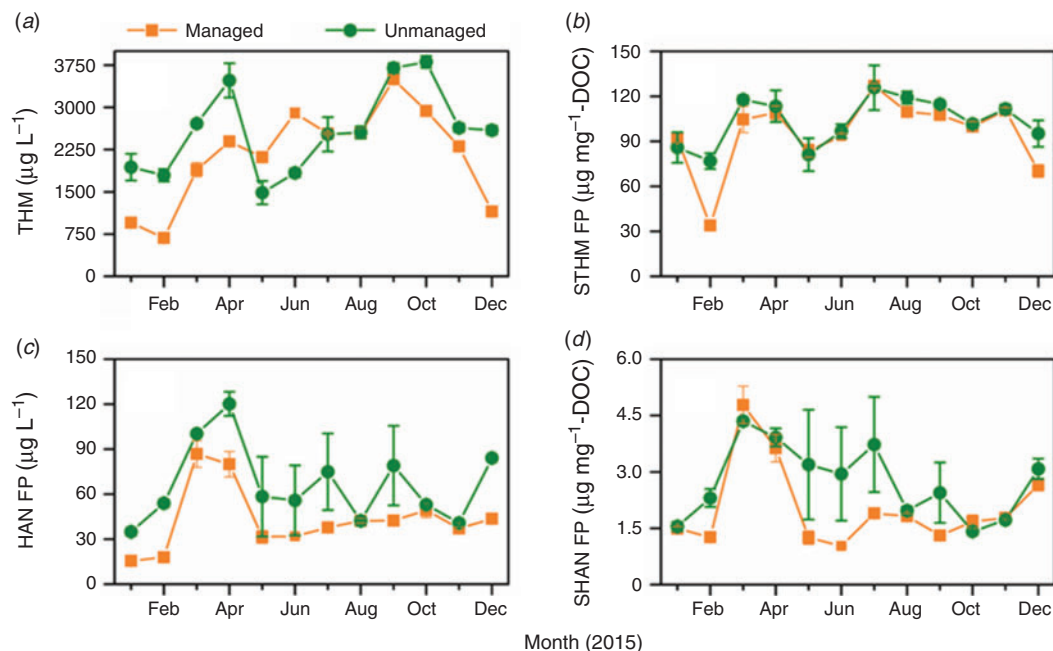
Fig. 4. Dissolved organic carbon (DOC, a), total dissolved nitrogen (TDN, b) and specific ultraviolet (UV) absorbance at 254 nm ( $SUVA_{254}$ , c) patterns during 1 year of sampling (2015). The blue and green lines represent the flow patterns (similar) at the managed and unmanaged watershed respectively.

affected by DOM quantity rather than quality (Chow *et al.* 2011; Majidzadeh *et al.* 2017; Ruecker *et al.* 2017).

HAN FP was also higher at the unmanaged watershed than at the managed watershed, but was statistically significant only in January, February, April, November and December ( $P < 0.05$ , Fig. 5). DOM reactivity to form HAN (i.e. SHAN FP) was similar between the two watersheds except for May, June and July, with higher reactivities in the unmanaged watershed. This pattern can be attributed to the higher aromaticity of DOM during those months for the unmanaged watershed. Multivariate regression analysis suggested that SHAN FP was positively linked to DOM aromaticity ( $P = 0.008$ ). In addition, higher HAN concentration and activity at the unmanaged watershed could be linked to our findings from pyrolysis GC-MS, which showed more nitrogenous aromatic compounds could be exported from the unmanaged watershed than from the managed watershed, especially from the duff layer.

This hypothesis was further confirmed through the laboratory extraction study, separating HAN and THM formation in





**Fig. 5.** Monthly changes in trihalomethanes (THMs, *a*) and haloacetonitriles (HANs, *c*) formation potentials (FP) and specific FP (normalised by dissolved organic carbon) of THM (*b*) and HAN (*d*) during 1 year of sampling (2015). STHM FP, specific THM FP; SHAN FP, specific HAN FP.

Watershed	Forest floor	Surface water quality	DBPs
Unmanaged (Watershed 80)	$12.3 \pm 1.1 \text{ Mg ha}^{-1}$ Litter mass	$21.94 \pm 1.8$ DOC ( $\text{mg L}^{-1}$ )	$2143 \pm 136$ THM-FP ( $\mu\text{g L}^{-1}$ )
	$5.8 \pm 1.6 \text{ Mg ha}^{-1}$ Duff mass	$0.9 \pm 0.08$ TDN ( $\text{mg L}^{-1}$ )	$43.0 \pm 4.2$ HAN-FP ( $\mu\text{g L}^{-1}$ )
Managed (Watershed 77)	$12.5 \pm 0.7 \text{ Mg ha}^{-1}$ Litter mass	$24.95 \pm 2.6$ DOC ( $\text{mg L}^{-1}$ )	$2667 \pm 192$ THM-FP ( $\mu\text{g L}^{-1}$ )
	$10.5 \pm 1.4 \text{ Mg ha}^{-1}$ Duff mass	$1.0 \pm 0.1$ TDN ( $\text{mg L}^{-1}$ )	$66.5 \pm 6.0$ HAN-FP ( $\mu\text{g L}^{-1}$ )

**Fig. 6.** Long-term forest management may alter long-term detrital mass and chemistry in favour of improved water quality by reducing dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentration, and thus, disinfection by-products (DBPs) formation potential (FP). The values (mean  $\pm$  standard deviation) represent the results from the field study. HAN, haloacetonitrile; THM, trihalomethane.

the litter and duff layers. The laboratory study showed that HAN FP in duff treatments was not similar between the two watersheds and the unmanaged watershed ( $588 \pm 38 \mu\text{g L}^{-1}$ ) had significantly higher HAN FP than the managed watershed ( $428 \pm 29 \mu\text{g L}^{-1}$ ,  $P = 0.008$ ). Reactivity of DOM-forming HAN (i.e. SHAN FP) was also higher (marginally significant at  $P = 0.07$ ) for the unmanaged watershed than for the managed watershed (Table 2). Average HAN FP for the litter treatments was similar between the two watersheds, but was 83% ( $\pm 6.7$ ) higher ( $954 \pm 66 \mu\text{g L}^{-1}$ ) than for the duff treatments ( $519 \pm 46 \mu\text{g L}^{-1}$ ,  $P < 0.001$ ). THM FP and DOM reactivity in the formation of THM (i.e. STHM FP) were not statistically different between the unmanaged and managed watersheds

(Table 2). Comparing the litter and duff treatments, THM FP was significantly higher with litter treatments ( $5303.1 \pm 425.8 \mu\text{g L}^{-1}$ ) than with duff treatments ( $3216.9 \pm 301.1 \mu\text{g L}^{-1}$ ,  $P < 0.001$ ), which could be related to higher DOC in the litter treatments. Normalising THM FP by DOC showed that the reactivity of DOM to THM (i.e. STHM FP) was similar in the litter and duff treatments (Table 2).

## Conclusion

Results from this study suggested that forest management may alter long-term detrital mass and chemistry in ways that improve water quality and lower DBP precursors (Fig. 6). The laboratory study showed that DOC, TDN, and  $\text{NH}_4^+\text{-N}$  export from

managed detritus were less than extracts from unmanaged detritus, most likely because of changes in detrital chemical composition caused by long-term management practices. Moreover, chemical group identification in water extracts revealed that more aromatic carbon and nitrogen were exported from unmanaged detritus than from managed detritus. Field study observations confirmed the laboratory study observations, suggesting that prescribed fire may alter long-term detrital mass and chemistry in favour of improved water quality, indicated by higher DOC, TDN and DOM aromaticity in the unmanaged watershed for most of 2015. DBP formation was also less in the managed watershed and was positively linked to DOM quantity and aromaticity. Minimum, maximum and average observed DOC, TDN and DBP formation were higher in the unmanaged watershed than in the managed watershed (Fig. 6). From our results, it appears that in many forested watersheds, the implementation of management practices, including prescribed fire, harvesting and understory mastication, may be necessary to improve human health, as well as forest health. This study adds to the list of forest management benefits that have been documented in the southeastern USA.

### Conflicts of interest

The authors declare no conflicts of interest.

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