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# Regional drivers of organic carbon age in lotic systems of the conterminous United States

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#### **Regional drivers of organic carbon age in lotic systems of the conterminous United States**

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Studies at Virginia Commonwealth University.

By

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### **Abstract**

Rivers play a critical role in global carbon (C) budgets despite their comparatively small surface area. A significant portion of the terrestrial C that they receive is transformed, re-mineralized, or stored during transit to the ocean. Radiocarbon  $(\Delta^{14}C)$  data show that a fraction of riverine organic C (OC) has been pre-aged in the terrestrial environment. Lateral export of carbon from these aged pools may contribute to atmospheric carbon dioxide emissions through microbial and photochemical oxidation. However, little is known about the regional climatic, anthropogenic, and landscape factors that promote the mobilization of aged OC to rivers. This study examines associations between riverine OC and river basin characteristics. It leverages data from two sources: 1) a spatially extensive collection of literature-reported  $\Delta^{14}$ C measurements and 2) the U.S. Environmental Protection Agency's Stream-Catchment (StreamCat) database. The radiocarbon data include 95 dissolved ( $\Delta^{14}$ C<sub>DOC</sub>) and 54 particulate ( $\Delta^{14}$ C<sub>POC</sub>) organic C measurements after averaging by location. We used the random forest (RF) machine learning algorithm to build independent models of  $\Delta^{14}C_{DOC}$  (MSR = 7319.51, % var explained = 17.05) and  $\Delta^{14}C_{POC}$  (MSR = 11254.03, % var explained = 45.36). In both RF models, the StreamCat data were used as predictor variables. Model validation was accomplished with a random, 75:25 split where 75% of the data were used for model building and the remaining 25% were used for testing and validation ( $\Delta^{14}$ C<sub>DOC</sub> RMSE = 61.23, r = 0.71;  $\Delta^{14}$ C<sub>POC</sub> RMSE = 39.82, r = 0.94). Key predictors of  $\Delta^{14}C_{DOC}$  were generally climactic or land cover variables affecting terrestrial primary productivity. Key predictors of  $\Delta^{14}C_{POC}$  were primarily factors associated with sediment transport and erosion, but also included several indicators of anthropogenic influence. Human activities appear to be destabilizing both C pools, resulting in aged C flux to the more rapidly cycled C reservoir in rivers.

### **Introduction**

Terrestrial organic carbon (OC) has three fates: long-term storage in biomass or physicochemical structures such as stable soil aggregates, oxidation (e.g., pyrolysis, combustion, gasification, and respiration), or export as dissolved or particulate organic carbon (DOC and POC) to inland waters. Of these, rivers serve as the only pathway between the terrestrial, oceanic, and atmospheric global C reservoirs. Traditional global C models recognize the importance of rivers as links between the terrestrial and oceanic reservoirs; however, only recent models incorporate them as biochemical reactors of C wherein C may be transformed, re-mineralized, or stored during transport (Cole et al., 2007; Battin et al., 2009; Aufdenkampe et al., 2011). Inputs of bulk terrestrial OC range from 1.9 to 2.7 petagrams per year (Pg C yr<sup>-1</sup>) (Cole et al., 2007; Battin et al., 2009; Tranvik et al., 2009), but only 0.9 Pg C  $yr^{-1}$  are estimated to reach the ocean (Cole et al., 2007) (Figure 1). Carbon dioxide  $(CO_2)$  evasion from in-stream processing of C is a globally significant source of atmospheric  $CO<sub>2</sub>$  (Battin et al., 2009; Raymond et al., 2013), with C residence times as short as days to weeks in some rivers (Battin et al., 2009). At the global scale, a growing number of studies show that many rivers transport highly aged terrestrial OC previously removed from the C cycle (see Marwick et al., 2015). This C may be oxidized by photodegradation (Caraco et al., 2010) or microbial processing (McCallister et al., 2012) and thus contribute an unknown amount of  $CO<sub>2</sub>$  to the atmosphere. This release of previously stored, aged C into the atmosphere is analogous to the burning of fossil fuels. Thus, investigating the factors that mobilize and deliver aged OC to fluvial systems may contribute not only to our understanding of riverine OC cycling, but may also have implications for climate change mitigation and CO<sub>2</sub> management.

The source and cycling of OC in rivers can be assessed through natural abundance of stable  $(\delta^{13}C)$  and radiocarbon (<sup>14</sup>C) of the different OC pools. The distributions of these isotopes in the environment are governed by predictable natural phenomena (i.e., fractionation, mixing, and radioactive decay), which enables their use as environmental tracers of aquatic OC in biogeochemistry studies (Fry, 2006). Radiocarbon provides unique information on the age of organic matter and is now regularly used to assess the mobilization of aged allochthonous C in aquatic systems (Raymond et al. 2001a,b; Hossler and Bauer, 2012; Butman et al., 2014;

Marwick et al., 2015). The analysis of the deviation of radiocarbon in parts per thousand (‰) from the isotopic ratio ( $\Delta^{14}$ C) is the common measure for comparing the <sup>14</sup>C of samples across different locations. This measure corrects <sup>14</sup>C content for fractionation effects using a  $\delta^{13}C$  value of -25 ‰ and expresses it relative to a known oxalic acid standard that represents the pre-nuclear atmospheric  ${}^{14}C$  of CO<sub>2</sub> in the base year of 1950 (Stuvier, 1977).

Riverine OC may range in age from modern (decadal) to  $> 1,000$  years old depending on the source and anthropogenic influences (Marwick et al., 2015). In paired riverine DOC and POC measurements, DOC typically has a more recent origin than POC (Marwick et al., 2015), reflecting terrestrial vegetation and surface soils as dominant DOC sources (Longworth et al., 2007). In general, natural terrestrial reservoirs from which aged (i.e.,  $^{14}$ C-depleted) DOC may be exported include groundwater (Moyer et al., 2013), peat-dominated systems (Schell, 1983), aged soil organic matter from deeper soil profiles (Butman et al., 2012), and shale outcrops (Raymond et al., 2004). Other studies have shown that permafrost (Neff et al., 2006) and precipitation (Raymond et al., 2005) may also contribute aged DOC to rivers. In situ processing of DOC along the fluvial continuum may result in the export of aged DOC to the ocean through the preferential utilization of younger DOC (Raymond and Bauer, 2001a; Raymond et al., 2004). Additionally, aged OC has also been reported in rivers fed by glacial meltwaters (Hood et al., 2009; Aiken et al., 2014), in the geologically ancient Kimberly region of Australia (Fellman et al., 2014), and in small mountainous rivers (SMRs, rivers with drainage basins  $< 10,000$  km<sup>2</sup> and headwater elevations > 1,000 m) (Milliman and Syvitski, 1992) such as the Santa Clara river (Masiello and Druffel, 2001).

In contrast to DOC, less than 20% of all riverine  $\Delta^{14}C_{POC}$  measurements suggest a modern origin (Marwick et al., 2015). Natural sources of aged POC include aged organic matter from deeper soil horizons or rock-bound OC (fossil POC or kerogen) derived from the physical and chemical erosion of carbonaceous rocks (Komada et al., 2004; Leithold et al., 2006). Aged POC is highly correlated with sediment yield (Leithold et al., 2006; Marwick et al., 2015) suggesting it is primarily controlled by physical erosion. SMRs and rivers in active margin basins are major sources of aged POC (Masiello and Druffel, 2001; Komada et al., 2004; Goñi et al., 2013), except where lower sediment yields allow modern plant-derived OC to dominate (Leithold et al., 2006; Hatten et al., 2012). However, aged POC has also been detected in rivers occurring on passive continental margins (Raymond and Bauer, 2001b; Longworth et al., 2007) and in major river systems such as the Mackenzie River Delta (Goñi et al., 2005). Both aged and contemporary riverine POC inputs may additionally enter deposition-resuspension cycles which promote further remineralization and aging (Newbold et al., 1982), particularly in river valleys and floodplains (Meade, 1996).

Anthropogenic landscape modifications have increased total terrestrial OC flux to inland waters by approximately 20% since the 18th century (Regnier et al., 2013). This increased OC flux from human activities includes the enhanced mobilization of aged C (Butman et al., 2014). Agricultural activities may destabilize deep soil profiles and mobilize aged OC (Raymond et al., 2004; Ewing et al., 2006; Longworth et al., 2007; Sickman et al., 2010; Butman et al., 2014; Butman et al., 2018). Landscape modifications and development may also release aged OC to the watershed by decreasing contemporary contributions from terrestrial plants (Lu et al., 2014), especially when high-productivity systems such as wetlands are destroyed (Raymond et al., 2004). Other anthropogenic impacts on riverine C age include petroleum-based agrochemicals and oils from non-point urban runoff (Sickman et al., 2010), municipal wastewater inputs (Griffith et al., 2009; Griffith and Raymond, 2011), and burning of fossil fuels which can contribute fossil POC inputs in the form of black carbon (Mitra et al., 2002). River impoundments increase water residence time and associated DOC age; however, dams frequently result in enhanced algal production of presumably modern OC which may mask the aged DOC signature (Hossler and Bauer, 2012).

A robust, empirical database of OC radiocarbon measurements is now available to study largescale factors that may regulate aged C inputs to rivers. Models using publicly available, continental-scale data have been used previously to examine how basin characteristics and land use effect riverine conditions or constituents (Manning et al., 2020). Previous studies have attempted to synthesize spatially diverse  $\Delta^{14}$ C measurements to assess such patterns (Raymond and Bauer, 2001b; Raymond et al., 2004; Butman et al., 2012; Butman et al., 2014; Marwick et al., 2015). However, understanding of the regional controls of riverine C age is still limited by the lack of in-depth analysis of  $\Delta^{14}C$  as a function of basin characteristics. This study combines >

520 literature-derived  $\Delta^{14}$ C measurements from rivers of the continental United States (CONUS) with the U.S. Environmental Protection Agency's Stream-Catchment (StreamCat) Database. StreamCat is a national database of watershed characteristics and associated disturbance indices for approximately 2.65 million stream and river segments (Hill et al., 2006). Separate random forest (RF) models (Breiman, 2001) of  $\Delta^{14}C_{\text{DOC}}$  and  $\Delta^{14}C_{\text{POC}}$  are built to investigate regionalscale drivers of OC age in lotic systems. Syntheses evaluating the regional drivers of riverine C age may allow for a more complete understanding of the general anthropogenic, geophysicochemical, and climatic controls affecting OC composition and age in rivers.

### **Methods**

#### **Radiocarbon data**

C data were compiled from 27 primary publications (Appendix S1). The compiled dataset includes 305  $\Delta^{14}$ C<sub>DOC</sub> and 217  $\Delta^{14}$ C<sub>POC</sub> measurements from lotic systems throughout the CONUS. Mean  $\Delta^{14}C_{DOC}$  and  $\Delta^{14}C_{POC}$  values were used when multiple measurements were reported at a given location. Radiocarbon values and sampling coordinates were obtained directly from the source papers, their supplementary tables, or from personal communications with the original authors. In several cases where explicit coordinates were not available, but publication figures were of sufficient detail and quality, locations were spatially interpolated. In one case,  $\Delta^{14}$ C data were presented in detailed figures but not in tabular or appendix form (Hossler and Bauer, 2012); here, data values were interpolated from the figures with WebPlotDigitizer (version 4.2) software. C measurements collected prior to 1995 were compiled from source papers when available but were ultimately excluded from the final analyses as many of the predictor variables used in the analyses represented landscape conditions for more recent years (e.g., 2000 and later).

Some radiocarbon measurements were originally reported in "fraction modern" (f<sub>M</sub>) units. These were converted to  $\Delta^{14}$ C using an equation modified from McNichol and Aluwihare (2007):

$$
\Delta^{14}C = 1000 \left[ f_M \exp^{-\lambda(y-1950)} - 1 \right] \tag{1}
$$

where *y* represents the year of sample collection and measurement and  $\lambda$  is the Libby decay constant ( $\lambda$  = 8033). As discussed by Marwick et al. (2015), year of sample collection and <sup>14</sup>C content measurement are not typically both reported and as such are assumed to be identical in this equation. Error resulting from this assumption is expected to be  $\leq 0.62$  ‰, representing a difference of approximately five years between sample collection and measurement.

#### **Predictor variables**

 $\Delta^{14}$ C sampling locations were linked to the 1:100,000 scale National Hydrography Dataset version 2 (NHDPlus V2; McKay et al., 2015) geospatial framework using location information provided in the source publications. Spatial analyses were performed with ArcGIS Pro 10 software (version 2.3.2, Environmental Systems Research Institute, Redlands California, USA). The NHDPlusV2 delineates individual stream segments based on local catchments and assigns each a "common identifier" (COMID) that can be used as a primary key to link these data (point locations) to the StreamCat data (linear stream/river segments). StreamCat metrics are available at both the local catchment (Cat) and watershed (Ws) scale, the latter of which represents the catchment itself in addition to the hydrologically connected upstream catchments that contribute flow to the catchment's stream segment (Figure 2). These metrics include anthropogenic variables such as agriculture, population density, and land cover percent imperviousness in addition to natural variables such as lithology, soil characteristics, and elevation (see Hill et al., 2016 for a complete list of available metrics). Some StreamCat metrics are also expressed as a 100-m stream buffer (Rp100) occurring within either the Cat or Ws scales, representing conditions immediately adjacent to (i.e., within 100 m of) the stream channel.

A total of 249 StreamCat variables were evaluated as potential predictors in  $\Delta^{14}$ C models. Missing values in the StreamCat dataset were imputed using the R package missForest (Stekhoven, 2013) prior to analysis. The missForest method is a nonparametric algorithm that uses a RF trained on the observed values of the data matrix to predict missing values. To improve data imputation performance, we removed from consideration any continuous variables with missing data that had five or fewer unique data values. Following imputation, some yearspecific StreamCat metrics were manipulated prior to modeling. StreamCat metrics that were specific to years after 2009 (e.g., percent impervious surface values for 2011) were omitted because the compiled  $\Delta^{14}$ C dataset does not include samples collected after 2009. Population density data from the 2010 decennial U.S. census were retained as this represented the only direct population measure within the dataset. For other StreamCat metrics where multiple years were included for a given variable (e.g., 2001 vs. 2006 National Land Cover Database values), an average value was calculated with one of two methods: (1) the weighted mean based on year of sample collection  $\pm 2$  years (for StreamCat metrics reported for non-continuous years); or (2) a simple mean where few years were represented (e.g., 2008 and 2009 Parameter-elevation Regression on Independent Slopes Model tables and 2008 and 2009 predicted stream temperature tables).

#### **Random forest models**

RF modeling (Breiman, 2001) was used to investigate the predictive importance of each StreamCat variable on  $\Delta^{14}$ C<sub>DOC</sub> and  $\Delta^{14}$ C<sub>POC</sub>. With large and complex datasets such as StreamCat, RFs can be advantageous because they are capable of (1) modeling high-order interactions among correlated predictor variables without overfitting, (2) handling non-linear relationships, and (3) maintaining accuracy when there are missing data (Cutler et al., 2007). RF models have been shown to match or outperform other common methods of classification and regression used in ecological and environmental applications (Prasad et al., 2006; Gislason et al., 2006; Cutler et al., 2007; Freeman et al., 2015).

RF is a modified bagged decision tree algorithm that fits decision trees on many bootstrap samples of the training dataset, then aggregates decisions from all trees within the model (collectively referred to as the forest) to make predictions. Each tree uses its own bootstrap sample, which contains approximately 0.33 of the original observations, which can be repeated at least once. It is this split-variable randomization that occurs during the bagging process that reduces tree correlation. In addition to using bootstrap samples, each tree works from a randomly-selected subset of the predictor variables. In the randomForest R package used in this study, this number is typically the total number of predictors divided by three (for regression

trees) or the square root of the total number of predictor variables (for classification trees) (Liaw and Weiner, 2002). This ensures that trees do not over rely on individual features and that all potentially predictive features are evaluated. Working from these variants of the training dataset, each tree behaves like a traditional decision tree, wherein data at each parent node are split into left and right child nodes based on which subset of the data has the smallest mean squared error (MSE). This occurs at subsequent nodes until the tree reaches the largest possible size, as defined by pre-set hyperparameters dictating the minimum number of observations allowed for a split or when the overall variance can no longer be reduced beyond a certain threshold. Model outcomes are determined using the mean (for regression) or most frequent (for classification) predictions aggregated across individual trees in the forest. The proportion of out-of-bag (OOB) data consisting of original observations excluded from the bootstrapped samples incorrectly predicted by the trees can be used to assess model accuracy (OOB error).

Predictor variable importance is measured during RF modeling by calculating variable influence on model performance when those variables are randomly permuted in individual trees (Breiman, 2001). Variable importance can be measured by computing the percent increase in mean squared error (%IncMSE) or by the increase in node purity (IncNodePurity). %IncMSE measures the increase in MSE that occurs as a result of the random permutation of a variable. IncNodePurity is calculated from the reduction in the sum of squared errors when a coefficient is chosen for a split. For both importance measures, higher values indicate that the coefficients have a greater degree of influence in the model.

Model selection approaches for RF may involve the stepwise reduction of input variables or tuning of key model parameters (e.g., number of trees in the forests and number of predictor variables selected at each node during tree growth). However, previous studies suggest that these approaches are unnecessary for RF models to remain robust (Cutler et al., 2007; Freeman et al., 2015; Fox et al., 2018). Furthermore, Fox et al. (2017) found that stepwise variable selection biased OOB accuracy and destabilized model predictions. For these reasons, we used the full StreamCat variable set in the RF models except for select omissions of variables discussed previously (see 'Predictor variables' above) and no additional tuning steps were taken beyond

setting the maximum forest size to 3,000 trees to stabilize the variable importance measures (Liaw and Weiner, 2002; Wang et al., 2006).

For model validation, 24  $\Delta^{14}C_{\text{DOC}}$  and 14  $\Delta^{14}C_{\text{POC}}$  measurements (25% of each dataset) were randomly queried and withheld during model creation. The remaining 75% of each dataset was used for model building while the test data were used to evaluate each model's predictive performance on the withheld sites'  $\Delta^{14}$ C measurements. All RF models were built and tested using R version 3.5.1 (R Development Core Team, 2018, Vienna, Austria) and the 'RandomForest' library (Liaw and Weiner, 2002).

### **Results**

After calculating the mean  $\Delta^{14}$ C by location and removing measurements collected prior to 1995, the compiled  $\Delta^{14}$ C dataset included 95  $\Delta^{14}$ C<sub>DOC</sub> and 54  $\Delta^{14}$ C<sub>POC</sub> measurements, representing a total combined watershed area of approximately  $37,283$  km<sup>2</sup>. The distribution of measurements from both pools across Eastern, Central, or Western U.S. were roughly similar and were concentrated in the Eastern and Western U.S. (Figure 3). The median signature for  $\Delta^{14}C_{DOC}$  was 34.17 ‰ (modern) while the median signature for  $\Delta^{14}C_{POC}$  was -74 ‰, corresponding to an age of approximately 550 years before present when calibrated to a 2009 collection and measurement date using equation 1 (Figure 4). The range of observed  $\Delta^{14}C_{DOC}$  values was -263.00-210.48 ‰ and the range of observed  $\Delta^{14}C_{\text{POC}}$  values was -526.50-94.9 ‰. We report RF regression model  $(n_{tree} = 3000, n_{mtry} = 83)$  results for  $\Delta^{14}C_{DOC}$  (MSR = 7319.51, % var explained = 17.05) and  $\Delta^{14}C_{\text{POC}}$  (MSR = 11254.03, % var explained = 45.36). OOB errors for the imputed predictor values are provided in Appendix S2. Quantile ranges for the StreamCat predictors and  $\Delta^{14}C$  for both pools are provided in Appendix S3.

The IncNodePurity variable importance measure was used to rank the 10 most influential  $\Delta^{14}$ C predictors (Figure 5). For the final variable importance model, only one variable from each set of related variables (Cat, WS, Rp100) was allowed to be included. RF results suggested that the  $\Delta^{14}$ C values for both OC pools were affected by a combination of natural and anthropogenic variables. Metrics characterizing natural influences comprised the majority of the top 10

predictors across both models. These natural influences included a variety of land cover, geophysicochemical and climate variables. However, no single class of StreamCat variable emerged as most influential for both  $\Delta^{14}C_{\text{DOC}}$  and  $\Delta^{14}C_{\text{POC}}$ . Percent woody wetland land cover within a 100-m of watershed streamlines and 2008-2009 average catchment precipitation levels were the most influential natural factors for  $\Delta^{14}$ C<sub>DOC</sub>. Watershed elevation, percent forest loss to fire within a 100-m buffer of the watershed streamlines, and percent barren land cover within a 100 m buffer of the watershed streamlines were the most influential natural factors for  $\Delta^{14}C_{POC}$ . Anthropogenic predictors characterizing development or agriculture were present in both models, but were more influential for  $\Delta^{14}C_{\text{POC}}$ , as indicated by changes in node purity.

For each model predictor, the direction of association (positive vs. negative) with carbon age was inferred from partial dependence plots (not shown). Predicted  $\Delta^{14}C_{POC}$  responded negatively to increases in all StreamCat coefficients except for watershed bedrock depth, whereas predicted  $\Delta^{14}$ C<sub>DOC</sub> response varied (Figure 5). Predicted  $\Delta^{14}$ C<sub>DOC</sub> response was positively associated with increases in coefficients representing land cover or climatic influences, apart from percent deciduous forest land cover. In most cases, anthropogenic predictors were associated with decreasing (older)  $\Delta^{14}$ C responses between models.

External validation of the models using the independent 25% test subset of the data showed that RF had lower predictive accuracy for  $\Delta^{14}C_{DOC}$  compared to  $\Delta^{14}C_{POC}$  (Table 1). There was a strong positive correlation between the predicted and observed values for both models  $(\Delta^{14}C_{DOC})$  $r = 0.71$ ,  $\Delta^{14}C_{POC}$  r = 0.94) (Figure 6). The DOC model appeared biased towards predicting modern  $\Delta^{14}$ C <sub>DOC</sub>, as indicated by deviation from the 1:1 prediction line. Similarly, there was a greater deviation from the 1:1 line where observed  $\Delta^{14}C_{\text{POC}}$  was more negative. For  $\Delta^{14}C_{\text{DOC}}$ , bias in the model predictions may be a result of having comparatively few aged  $\Delta^{14}C$  poc measurements in the original dataset available for training. Deviations between predicted and observed  $\Delta^{14}$ C <sub>POC</sub> measurements may have been induced by the presence of several highly aged  $\Delta^{14}$ C <sub>POC</sub> measurements (< -250 ‰), none of which were included in the testing dataset during the random 75:25 split prior to model creation.

### **Discussion**

Fluvial OC is a complex mixture of compounds with a range of ages determined by regional climate and landscape features. While the number of  ${}^{14}C$  measurements is increasing, there remain significant gaps in both the geographic coverage and equivalence of measurements across river sizes (Marwick et al., 2015). Robust models are necessary to achieve a comprehensive understanding of regional drivers of riverine OC age and lay the foundation for future interpolation of OC ages where  $^{14}$ C data are sparse.

In this model, both natural and anthropogenic predictors were influential drivers of riverine particulate and dissolved OC age. Previous research has suggested that anthropogenic disturbance is critical for the mobilization of aged terrestrial POC and DOC (Butman et al., 2015; Hossler and Bauer, 2012; Marwick et al., 2015). Basin level syntheses of OC age have suggested the liberation of ancient terrestrial OC results from agricultural based tilling, mechanical weathering of underlying lithology, and inputs of fossil-fuel-derived OC (Sickman et al., 2010; Longworth et al. 2007; Griffith and Raymond, 2009; Hossler and Bauer, 2012). However, these studies have been unable to distinguish the source of fossil-derived inputs (i.e., wastewater treatment plants (WWTPs), pesticides, synthetic fertilizers, petroleum) contributing to the aged riverine OC signature (Butman et al., 2015).

Relative to the data platforms employed for existing models of riverine OC age (Butman et al., 2012; Butman et al., 2015; Hossler and Bauer, 2012; Longworth et al. 2007; Lu et al., 2014), StreamCat provided a more comprehensive accounting of potential point and non-point sources of ancient fossil-derived C sources (e.g., proximity to WWTPs, Superfund sites, watershed pesticide application). Our model identified multiple anthropogenic factors associated with the presence of aged OC along the riverine continuum. For example, urbanization intensity and roads (density of roads or density of road-stream intersections for DOC and POC, respectively) were among the most influential predictors of aged C for both pools. Similarly, Butman et. al. (2015) found increased watershed disturbance to be negatively correlated with radiocarbon age of DOC from 77 small watersheds  $( $400 \text{ km}^2$ )$  worldwide. Our findings further suggest that petroleum run-off from impermeable surfaces is the primary source of fossil fuel-derived OC to fluvial OC rather than point sources such as WWTP (Griffith and Raymond, 2009) and pesticides from agricultural run-off (Butman et al., 2014).

For POC, the model additionally indicated canal density and forest loss from fire as significant drivers of age. Although the mechanism for the relationship between aged POC and canals is uncertain, this may be an indirect effect of irrigation-induced erosion along the banks or streambeds of gravity irrigation systems (U.S. Department of the Interior, 2018). Water diverted into a canal from reservoirs may additionally contain previously buried sediment POC (Maavara et al., 2017). Wildfires increase erosion and downstream suspended sediment and POC (Meixner & Wohlgemuth, 2004) and produce black carbon (BC). Black carbon is a largely recalcitrant byproduct of incomplete combustion of terrestrial OC which can be exported to rivers or remain in soil stores to be pre-aged prior to release in future disturbance events (Czimczik & Masiello, 2007; Hanke et al., 2017; Coppola et al., 2018).

Anthropogenic influences were primarily negative drivers of OC age with one exception: the percentage of hay and pasture within the watershed. Land cover conversion from forest to agriculture typically results in an overall reduction of soil C stocks (Post and Kwon, 2000). Tillage increases the mean age of surface soil OC through mixing with deeper older profiles (Longworth et al., 2007) while decreasing soil permeability, increasing soil aeration and erosion, and decreasing DOC exports (Follett, 2001; Lal, 2003). In contrast, some pasture and grassland management practices promote supplements of soil OC to aid restoration efforts in severely degraded areas (Machmuller et al., 2015). In addition, it has become common practice to enhance pasture soil fertility through additions of poultry litter, generating significant manurederived OC inputs from grazing cattle (Molinero and Burke, 2009). Consequently, run-off from pastures would result in the leaching and substantial export of contemporary DOC relative to other anthropogenic land use types (Seitzinger et al, 2002; Molinero and Burke, 2009).

Increased precipitation, atmospheric N deposition, and wetland coverage were all associated with younger fluvial DOC in our model. Wetlands have been documented to export significant amounts of DOC (Mulholland, 1997) with a modern  ${}^{14}C$  signature (Raymond and Hopkinson, 2003; Raymond et al., 2004) to adjacent streams and rivers as a result of shallow flow paths

through organic rich soil horizons. Contemporary OC subsides to aquatic systems are associated with increased terrestrial NPP which is driven by both enhanced precipitation and inorganic nitrogen wet deposition (Ollinger et al., 2002; Aber and Magill, 2004). However, the role of precipitation itself on age of OC export is not limited simply to its association with greater NPP. Discharge is one of the most significant drivers of allochthonous C delivery to watersheds due to its effects on runoff and erosion (Lauerwald et al., 2012; Hossler and Bauer, 2012). Under high flow conditions, contemporary OC contributions generally increase (Neff et al., 2006) due to shallower flow paths and leaching of surface litter (Barnes et al., 2018). Under baseflow conditions and in more arid environments  ${}^{14}$ C-depleted contributions from deeper soil profiles and groundwater comprise the majority of flow (Sanderman et al., 2009; Butman et al, 2012; Barnes et al., 2018).

In general, the radiocarbon age of POC was primarily influenced by erosional and transport processes. Discharge-driven suspended sediment yield can be a significant driver of aged  $\Delta^{14}$ C<sub>POC</sub> (Komada et al., 2004; Leithold et al., 2006). However, in our model, precipitation was not one of the influential predictors for  $\Delta^{14}C_{POC}$ . This may be due to contrasting compositions of suspended sediment loads across watersheds, which may vary from surficial contemporary organic-rich fractions to fossil POC from bedrock erosion in SMRs (Rosenheim et al., 2013; Marwick et al., 2015). The negative relationship between  $\Delta^{14}C_{POC}$  and bedrock depth suggests that mechanical weathering and erosional processes are the primary drivers of aged POC export. Furthermore, watershed elevation was identified as the most influential predictor for  $\Delta^{14}C_{POC}$  in this study, reinforcing the relationship between aged POC mobilized by SMRs.

The RF approach used in this study confers an advantage over traditional linear modeling approaches through its ability to model complicated relationships among correlated environmental variables. However, while external validation resulted in a strong correlation between predicted and observed  $\Delta^{14}$ C, it's possible that model performance for both OC pools could be improved by adding a temporal dimension to the study. Intra-basin temporal variation in discharge, vegetation phenology, and anthropogenic activities may have significant effects on C flux, composition, and age in some rivers (Neff et al., 2006; Sanderman et al., 2009; Aiken et al., 2014). However, a study of the Parker River watershed by Raymond and Hopkinson (2003)

did not find a difference between DOC age or concentration between high-flow and low-flow measurements. Although some temporal  $\Delta^{14}C$  data were available in the source publications, this was not the case for many locations and modeling is still limited by the lack of complementary temporal data for many of the potential drivers.

Another possible caveat to this approach is that many of the primary publications sourced in this study characterize  $\Delta^{14}$ C on the East Coast, at only one or two locations within a basin (Figure 3). Increased longitudinal sampling should help discern downstream changes in  ${}^{14}C$  arising from instream processes, such as DOC mineralization, *in situ* phytoplankton production and storage in streambeds, or behind impoundments (Raymond and Bauer, 2001a; Mayorga et al., 2005; Butman et al., 2015) . Increased inter-basin sampling across the CONUS could further enhance RF model accuracy and may allow for the separation of significant drivers among different ecoregions or major basins. For instance, basin size can obfuscate potential drivers of C age (Butman et al., 2015).

Our study is one of only a few to assess the influence of basin characteristics on organic riverine  $\Delta^{14}$ C at a national scale, with most previous syntheses focused on  $\Delta^{14}$ C<sub>DOC</sub>. Our results suggest that the controls on  $\Delta^{14}$ C vary between the OC pools. The significant drivers of  $\Delta^{14}$ C<sub>DOC</sub> were generally climactic or land cover variables affecting terrestrial primary productivity and the significant drivers of  $\Delta^{14}$ C<sub>POC</sub> were generally factors affecting sediment transport and erosion. However, human activities appear to be destabilizing both C pools, resulting in aged C flux to the more rapidly cycled riverine C pool. Although this study advances our understanding of the relative importance of the natural and anthropogenic basin characteristics affecting aged C inputs to rivers at a regional scale, the analytical power of future RF models could be improved by increased inter- and intra- basin  $\Delta^{14}$ C measurements and increased reporting of ancillary parameters (e.g.,  $\delta^{13}$ C ratios, bulk OC concentrations, inorganic C concentrations and age, and size fractions) which can provide additional insight on C composition and sources.

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## **Tables**

**Table 1**. Root mean squared error (RMSE) and mean absolute error (MAE) of the random forest model predictions applied to the test  $\Delta^{14}$ C<sub>DOC</sub> and  $\Delta^{14}$ C<sub>POC</sub> datasets.

	<b>RMSE</b>	<b>MAE</b>
$\Delta^{14}C_{\text{DOC}}$	61.23	54.29
$\Delta^{14}C_{\rm POC}$	39.82	32.62

## **Figures**



**Figure 1**. Rivers connect the terrestrial, oceanic, and atmospheric C reservoirs. All numbers are C fluxes in units of petagrams per year (Pg C  $yr^{-1}$ ) based on values reported by Battin et al. (2009). Figure adapted from Aufdenkampe et al. (2011).



**Figure 2**. A hypothetical watershed from the U.S. Environmental Protection Agency's Stream-Catchment (StreamCat) dataset. Each stream segment (blue lines) is delineated by a local catchment (dashed outline) representing the topography where precipitation falling on the land surface flows into that stream segment. All catchments within the watershed (green outline) flow to the most downstream catchment. In this study, radiocarbon sampling site were spatially related to the specific stream segment where sampling occurred using the stream segment common identifier (COMID).



**Figure 3.** Distribution of riverine  $\Delta^{14}C_{\text{DOC}}$  (n = 95) and  $\Delta^{14}C_{\text{POC}}$  (n = 54) measurements after removing measurements collected prior to 1995. Measurement distributions are shown in the context of water resource regions (HUC2 boundaries) and U.S. regions (Eastern, Central, and Western).



**Figure 4.** Frequency distribution plots for riverine  $\Delta^{14}C_{DOC}$  (top) and  $\Delta^{14}C_{POC}$  (bottom) in the continental United States (CONUS) from the compiled dataset, after calculating the mean  $\Delta^{14}C$ by location (when multiple measurements were collected at a given location) and removing measurements collected prior to 1995.



**Figure 5.** Importance plots for  $\Delta^{14}C_{DOC}$  (top) and  $\Delta^{14}C_{POC}$  (bottom) variables (variable description [StreamCat variable name]) ranked by increase in node purity and symbolized based on generalized categories of influence. Each variable represents the local catchment (Cat) or watershed (Ws) scale, occasionally within a 100-m buffer of the streamline within that scale (Rp100) as indicated by the suffix on the StreamCat variable name. Land use and land cover coefficients represent the mean value at a location for years  $\leq$  2009. Positive (+) or negative (-) signs indicate the direction of the relationship between predicted  $\Delta^{14}$ C and the coefficient by partial dependence plots.



**Figure 6.** Comparison of predicted and observed  $\Delta^{14}$ C values for each organic carbon (OC) pool, where r equals the Pearson correlation coefficient and the dotted line indicates where  $Y = X$ . Model validation consisted of a test subset (25%) of the original data excluded during model development.

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#### **Spatial data sources**

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## **APPENDIX S2. Imputed predictor OOB values**



Root mean squared error (RMSE) values for the imputed StreamCat coefficients, with n signifying the number of locations with missing data requiring imputation.







## **APPENDIX S3. Variable quantiles**

U.S. Environmental Protection Agency Stream-catchment (StreamCat) predictor (n = 249) variable quantiles for each OC pool.

























## **Vita**

Kaycee Faunce graduated in 2014 from the University of Mary Washington with a bachelor's degree in biology and a minor in environmental sustainability. In 2018, she earned a graduate certification in geographic information systems from Virginia Commonwealth University. She has a research background in wildlife ecology, psychopharmacology, and geography. She currently works as a geographer at the U.S. Geological Survey Virginia and West Virginia Water Science Center.