

1 **Title: Changes in global groundwater organic carbon driven by climate change and**  
2 **urbanization**

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22

23 **Abstract:** Climate change and urbanization can increase pressures on groundwater  
24 resources, but little is known about how groundwater quality will change. Here, we rely on a  
25 global synthesis (n = 9,404) to reveal the drivers of dissolved organic carbon (DOC), which  
26 is an important component of water chemistry and substrate for microorganisms which

27 control many biogeochemical reactions. Groundwater ions, local climate and land use  
28 explained ~ 31% of observed variability in groundwater DOC, whilst aquifer age explained  
29 an additional 16%. We identify a 19% increase in DOC associated with urban land cover.  
30 We predict major groundwater DOC increases following changes in precipitation and  
31 temperature in key areas relying on groundwater. Climate change and conversion of natural  
32 or agricultural areas to urban areas will decrease groundwater quality and increase water  
33 treatment costs, compounding existing threats to groundwater resources.

34

35 **Main Text:** Groundwater is the largest global source of fresh water. The potability of  
36 groundwater is highly dependent upon the concentration of dissolved organic carbon (DOC)  
37 due to its ability to alter water chemistry and microbial abundances <sup>1, 2, 3, 4, 5, 6</sup>. Over 100,000  
38 lifetime cancer cases in the United States (U.S.) can be attributed to contaminants in  
39 drinking water. A large proportion of the risk identified is associated with the presence of  
40 disinfection by products (DBPs) and arsenic <sup>7</sup>, both of which are strongly linked to DOC <sup>3, 8, 9,</sup>  
41 <sup>10, 11</sup>. Chlorination and ozonation used for water treatment can result in harmful by-products  
42 including 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone, brominated acetic acid,  
43 trihalomethanes (THMs), formaldehyde, halogenated acetic acids, due to the presence of  
44 organic matter <sup>12</sup>. These by-products can be genotoxic, carcinogenic or result in tumors <sup>12</sup>.  
45 Since most of the health impacts caused by dissolved organic matter (DOM) are related to  
46 the formation of by-products and depend on the concentrations of other water chemical  
47 parameters, the World Health Organization <sup>12</sup> and many countries including Australia <sup>13</sup> do  
48 not regulate total organic carbon (TOC) or DOC concentrations in drinking water directly but  
49 many countries such as USA <sup>14</sup>, Canada <sup>15</sup>, France <sup>16</sup>, China <sup>17</sup> and South Africa <sup>18</sup> highlight  
50 potential concerns related to THM formation, health effects and aesthetic quality in the broad  
51 DOC range of 0 - 5 mg L<sup>-1</sup> during treatment.

52

53 In addition to health and aesthetic impacts, the presence of DOC in water can lead to  
54 membrane fouling after ozonation. In order to avoid this, a biological filtration step is advised

55 to be added to the water treatment process for water containing DOC concentrations > 1 mg  
56 L<sup>-1</sup> <sup>19</sup>. This indicates that even relatively small DOC increases in raw groundwaters can have  
57 impacts not only on human health and water aesthetics, but also on the ease and cost of  
58 water treatment. High DOC concentrations can also increase the mobility of other  
59 contaminants in groundwater, including heavy metals and nutrients, by complex association  
60 with dissolved or colloidal organic matter (OM) <sup>3</sup>.

61

62 Climate variables such as temperature and precipitation impact on net primary production  
63 and microbial activity in ecosystems <sup>20,21</sup>. This drives availability of vegetation and its  
64 decomposition to DOC <sup>21,22</sup>. Changed precipitation, increasing temperatures and  
65 evaporation rates and patterns under future climate change scenarios are expected to alter  
66 biomass, impact surface water quantity <sup>23</sup>, and subsequently increase domestic and  
67 agricultural reliance on groundwater resources. Increasing reliance on groundwater due to  
68 climate change impacts may be compounded by urbanization and global population growth  
69 which is expected to increase groundwater contamination<sup>24</sup>. Recent research has focused  
70 on how climate change and urbanization will change groundwater quantities <sup>25,26</sup>, however  
71 understanding the impact of climate change and urbanization on the quality of our freshwater  
72 resources is also important <sup>23,27</sup>. Establishing links between climate change and  
73 groundwater quality requires large datasets to produce meaningful global estimates.

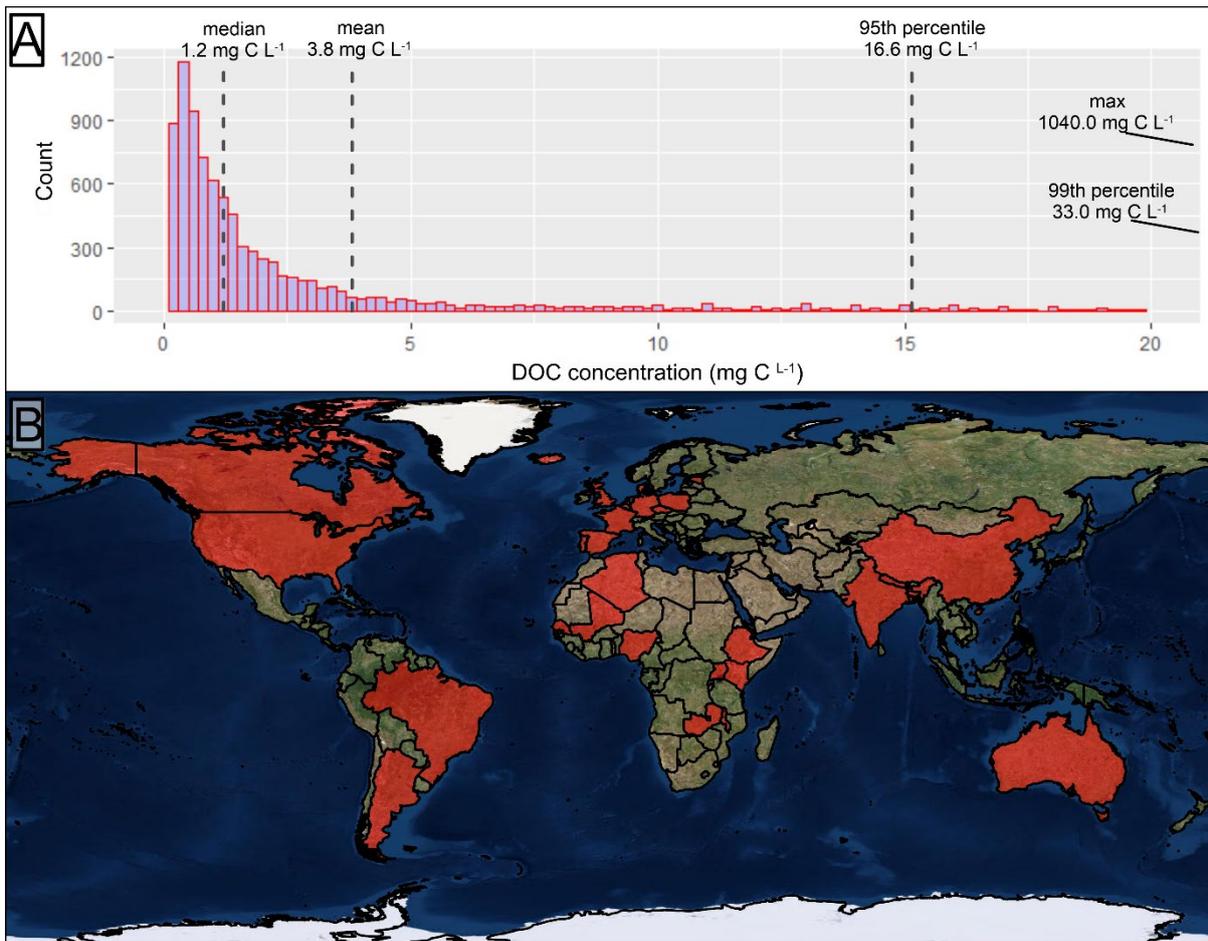
74

75 Here, we quantify the change in groundwater DOC related to climate change and urban land  
76 cover. We present the largest global dataset of 9,404 published and unpublished  
77 groundwater DOC concentrations (Table S1) obtained from aquifers in 32 countries across 6  
78 continents (Fig. 1). We provide an analysis of global groundwater DOC concentrations and  
79 quantify its key drivers. Specifically, we forecast changes in DOC concentrations due to  
80 projected changes in temperature and precipitation, as well as potential increases as a result  
81 of urban land use.

82

83 **Global groundwater DOC distributions**

84 Groundwater DOC concentrations vary spatially and are usually lower than surface water  
85 concentrations. The global mean, median and standard deviation of groundwater DOC  
86 concentrations are 2.7, 1.0 and 15.1 mg C L<sup>-1</sup> respectively (Fig. 1). Fig 1A shows that most  
87 groundwater DOC concentrations fall within the 0 – 5 mg C L<sup>-1</sup> range, with 84.1% of samples  
88 less than 5 mg C L<sup>-1</sup>, with the dataset largely dominated by countries in low and mid  
89 latitudes.



90

91 **Fig. 1.** A) histogram showing median global groundwater DOC concentrations (mg C L<sup>-1</sup>).

92 Sample sizes for individual countries ranged from 5 to 5,812, with 14 out of 32 countries

93 having  $n < 30$ . We have therefore presented aggregated data. Samples above 20 mg C L<sup>-1</sup>

94 are not included in the graph for visual clarity ( $n = 337$ ). The black dashed lines indicate the

95 global median (1.2 mg C L<sup>-1</sup>) and mean (3.8 mg C L<sup>-1</sup>) and 95th percentile ((16.6 mg C L<sup>-1</sup>)

96 values respectively. Also shown are the 99th percentile value and the maximum value (33.0

97 and 1040.0 mg C L<sup>-1</sup> respectively). B) countries from which groundwater DOC data was  
98 obtained.

99  
100 Variations in DOC concentrations between countries (Fig. 1) are likely to be related to  
101 recharge rates and aquifer types. World-wide Hydrological Mapping and Assessment  
102 Programme (WHYMAP) data <sup>28</sup> suggests that within the U.S. dataset (Fig. S1 <sup>29</sup>), major  
103 groundwater basins contain significantly lower DOC concentrations than local and shallow  
104 aquifers, and complex hydrogeological structures (both  $p < 2.2 \times 10^{-16}$ , Fig. S2). Therefore,  
105 groundwater age and depth seem to control groundwater DOC. There are also significantly  
106 higher DOC concentrations identified in aquifers with  $< 100 \text{ mm year}^{-1}$  recharge compared to  
107 those with high recharge rates ( $100 - 300 \text{ mm year}^{-1}$ ,  $p = 2.342 \times 10^{-7}$ ) and very high  
108 recharge rates ( $> 300 \text{ mm year}^{-1}$ ,  $p = 4.857 \times 10^{-5}$ , Fig. S2), which could indicate a dilution  
109 effect.

110

### 111 **Groundwater DOC controls**

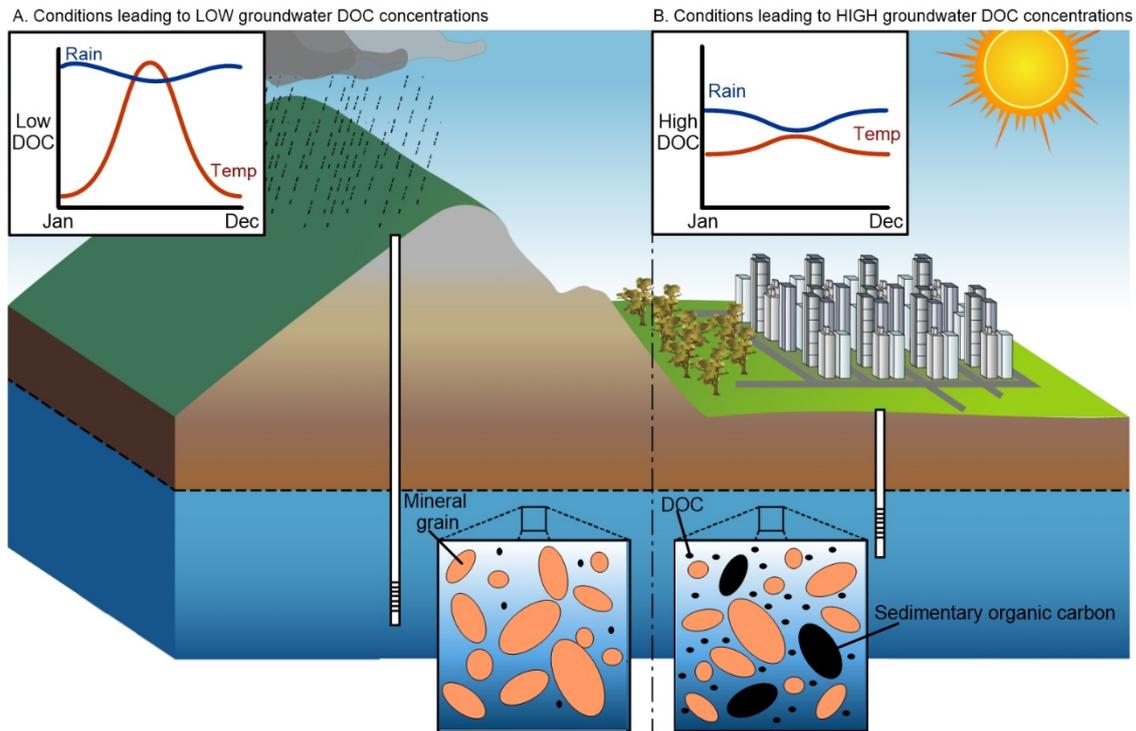
112 To determine the drivers of global DOC concentrations in groundwater, we generated a  
113 linear mixed model (Table S2) for a large dataset ( $n = 2,196$ ) collected by the National Water  
114 Quality Assessment (NWQA) program of the U.S. Geological Survey (USGS) <sup>29</sup>. This  
115 dataset was selected as it contained supplementary data including chemical parameters  
116 unavailable for other samples. This allowed us to extract supplementary climatic data <sup>30</sup>,  
117 water table depth <sup>31</sup> and land use data <sup>32, 33</sup> for analysis in the model.

118

119 Overall, the model explained 47.7% of the variation in DOC concentrations, with 31.3%  
120 explained by the fixed factors alone (all fixed and random factors), and 16.3% explained by  
121 the random factor aquifer age (age of host rock). Our analysis (Fig. S3, Table S2) shows  
122 positive correlations between DOC and temperature in the wettest quarter of the year ( $p < 2$   
123  $\times 10^{-16}$ ), groundwater temperature ( $p < 2 \times 10^{-16}$ ), and dissolved calcium (Ca) ( $p < 2 \times 10^{-16}$ ),  
124 potassium (K) ( $p = 2 \times 10^{-13}$ ) and iron (Fe) ( $p < 2 \times 10^{-16}$ ). There was also a weaker

125 relationship between DOC and manganese (Mn) ( $p < 0.039$ ). We also found negative  
126 relationships between DOC and temperature in the warmest quarter of the year ( $p < 2 \times 10^{-16}$ ),  
127 precipitation in the driest month of the year ( $p = 0.001$ ), silica (Si) ( $p = 2 \times 10^{-6}$ ), pH ( $p =$   
128  $4.06 \times 10^{-5}$ ), sample depth below land surface ( $p < 2 \times 10^{-16}$ ), land elevation ( $p = 1 \times 10^{-6}$ )  
129 and dissolved oxygen (DO) ( $p < 2 \times 10^{-16}$ ). Our analysis also shows negative relationships ( $p$   
130  $< 0.01$ ) between DOC and sodium (Na) ( $p = 0.001$ ), and DOC and precipitation in the wettest  
131 month of the year ( $p = 0.001$ ). Areas of urban land use were identified as having 19% higher  
132 groundwater DOC concentrations than natural or agricultural areas. Water table depth as a  
133 variable improved the overall model fit, however it is not a significant predictor of DOC  
134 concentrations ( $p = 0.071$ ). The factors correlated with decreased and increased  
135 groundwater DOC concentrations are presented in Fig. 2. While the model represents large  
136 scale relationships between DOC and control variables, these relationships can vary on a  
137 site by site basis due to site specific variables. Our model implies that large scale  
138 groundwater DOC concentrations are determined by the interaction of four major controlling  
139 factors: (1) climate (2) urban land-use (3) water chemistry (redox controls), and (4) aquifer  
140 age and groundwater residence times (Fig. 3).

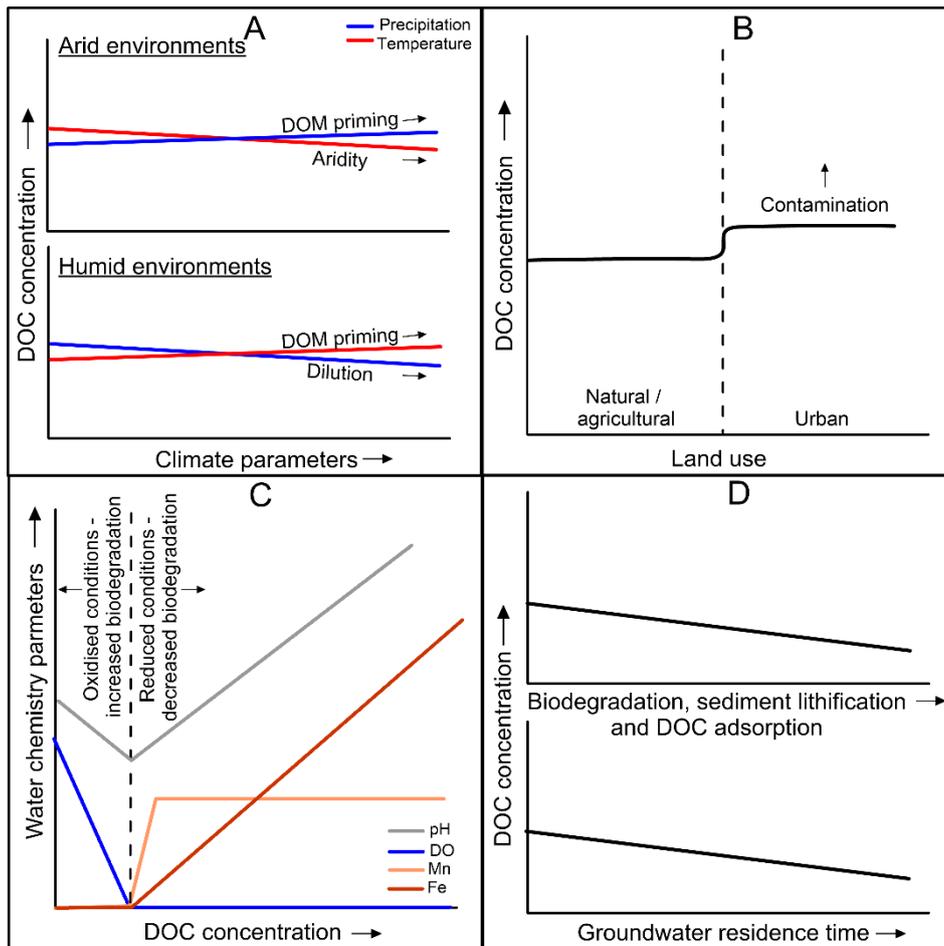
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142

143 **Fig. 2.** Factors and processes leading to low (A) or high (B) groundwater DOC  
 144 concentrations. Factors negatively correlated with groundwater DOC concentrations include  
 145 increasing pH, DO, Na and Si, precipitation in the wettest and driest months, temperature in  
 146 the warmest quarter, sample depth, elevation and aquifer age. Factors positively correlated  
 147 with groundwater DOC concentrations include Mn, Ca, Fe, and K, groundwater temperature  
 148 and temperatures in the wettest quarter. Urban land use was found to be 18% and 19%  
 149 higher in groundwater DOC concentrations than agricultural and natural land uses  
 150 respectively.

151



152

153 **Fig. 3.** Conceptual model showing the mechanisms for change in groundwater DOC  
 154 concentrations. (A) Climate parameters: in arid climates, groundwater DOC concentrations  
 155 increase with increased precipitation due to the priming of organic matter by microbes under  
 156 warm and increasingly wet conditions. Increased temperatures in arid environments lead to  
 157 decreased groundwater DOC due to increasing aridity. Increased precipitation in humid  
 158 environments decreases groundwater DOC concentrations due to dilution whilst increased  
 159 temperatures increase DOM priming by microbes. (B) Urban land use contributes to  
 160 groundwater DOC through contamination, for example through leaking septic and  
 161 sewer systems. (C) Water quality parameters and groundwater DOC concentrations are  
 162 linked and are largely controlled by redox conditions (NB: C shows variables where DOC is  
 163 the driver for the observed changes in water chemistry). (D) Increasing aquifer age results in  
 164 a decline in groundwater DOC due to sediment lithification and a depletion of sedimentary  
 165 organic matter over time. Increasing groundwater residence times lead to decreasing DOC

166 by a combination of filtration of DOC through smaller aquifer pore sizes and adsorption  
167 (where residence times correspond to longer flow paths), and increased exposure to  
168 biodegradation over time.

#### 169 170 **Climate controls**

171 Temperature and precipitation play an important role in predicting groundwater DOC  
172 concentrations. Overall, DOC decreases by  $9.5 \pm 1.1\%$  for every 10 mm increase in  
173 precipitation in the driest month of the year and decreases by  $2.5 \pm 0.8\%$  for every 10 mm  
174 increase in precipitation in the wettest month of the year. This is likely due to a dilution effect  
175 whereby accumulated soil DOM infiltrates the aquifer during initial rainfall and is later diluted  
176 by additional rainfall<sup>34</sup>. In arid climates, some of these trends may be reversed (Fig. 3). For  
177 example, a decrease in aridity represented by decreased temperature and increased  
178 precipitation, would increase groundwater DOC concentration since the precipitation in the  
179 wettest month of the year is not enough to cause significant dilution. Furthermore, in arid  
180 climates, groundwater DOC concentrations would be low due to the high temperatures and  
181 low rainfall leading to limited vegetation cover and bioavailable DOM<sup>35</sup>. We observed these  
182 trend reversals in linear analyses for the smaller Australian dataset ( $n = 79$  after removing  
183 incomplete data).

184

185 The model shows an overall groundwater DOC concentration increase by  $3.4 \pm 0.3\%$  for  
186 every 1 °C increase in average air temperatures in the wettest quarter of the year and  $4.6 \pm$   
187  $0.5\%$  for every 1 °C increase in sample groundwater temperature. In contrast, groundwater  
188 DOC concentrations decrease by  $8.9 \pm 1.1\%$  for every 1 °C increase in temperatures in the  
189 warmest quarter of the year. The source of DOC is dependent upon availability of water. In  
190 humid climates, increases in mean surface temperature in the wettest quarter of the year  
191 and increased groundwater temperatures are likely to cause increased temperatures in the  
192 soil zone. Under conditions of increased soil moisture, warm temperatures can stimulate  
193 biological activity, DOM priming<sup>36</sup>, and an increase in groundwater DOC.

194

## 195 **Water chemistry**

196 In the saturated zone, redox conditions and pH are strongly related to DOC concentration,  
197 with DOC concentrations  $9.2 \pm 2.4\%$  lower for each unit increase in pH, and  $6.8 \pm 0.6\%$   
198 lower with every  $1 \text{ mg L}^{-1}$  increase in DO. We also observe a  $4.5 \pm 0.4\%$  increase in DOC  
199 associated with a  $10 \text{ mg L}^{-1}$  increase in Ca. The smaller Australian dataset ( $n = 79$ ) also was  
200 consistent with the larger U.S. dataset ( $n = 2,916$ ) (see Supplementary Methods). The  
201 mineralization of DOC via biodegradation consumes DO, produces  $\text{CO}_2$  and hence carbonic  
202 acid, which causes a decrease in pH and related calcite dissolution and dissolved Ca  
203 production. Once conditions become anoxic and biodegradation rates are reduced, pH levels  
204 increase. The relationship between DOC and Ca, as well as microbial respiration by-  
205 products such as ammonium has been observed in regional-scale studies <sup>3</sup>.

206

207 We also show that reduced dissolved species of Fe(II) and Mn(II) are positively correlated  
208 with DOC concentrations. This trend may be explained by microbial use of Mn- and Fe-  
209 oxides as alternative electron acceptors to DO in the presence of DOC under anoxic  
210 conditions <sup>37</sup>. Aerobic microbes metabolize carbon at a faster rate than anaerobic microbes,  
211 therefore a lack of DO limits DOC biodegradation rates. Fe can accumulate within oxic  
212 sediment layers due to oxidation and precipitation of dissolved Fe in young sediments <sup>38</sup>.  
213 This Fe can become coated with OM and re-dissolve under reduced conditions releasing the  
214 OM, which can increase Fe with increased DOC. Decreased sulphate ( $\text{SO}_4$ ) and chloride  
215 (Cl) deposition due to recent emission regulations cause increases in DOC concentrations in  
216 surface waters <sup>39</sup> which could also lead to increased DOC concentrations in shallow  
217 groundwaters.

218

## 219 **Aquifer age and groundwater evolution**

220 The age of the geological formation, or aquifer age, explained 16.3% of variability in  
221 groundwater DOC. Groundwater in younger aquifers of Cenozoic sediments contained 41%

222 higher DOC concentrations than older Mesozoic and Paleozoic Era aquifers which support  
223 previous observations in smaller datasets <sup>4</sup>. Despite site specific observations of high  
224 groundwater DOC associated with older aquifers <sup>40</sup>, the model suggests sedimentary OM in  
225 young aquifers is more likely to be mobilized than in older, lithified aquifers. Other studies  
226 have also reported higher groundwater DOC concentrations originating from the matrix of  
227 younger aquifers <sup>41, 42</sup>.

228

229 We also observed a decrease in groundwater DOC concentrations of  $7.7 \pm 0.6\%$  for every  
230 10 m increase in sample depth. As DOC moves through porous media it undergoes filtration  
231 and oxidation to DIC. Consolidated sediment pore-throat sizes can occur in sizes much  
232 smaller than DOC, which is defined as the fraction of total organic carbon being able to pass  
233 through a membrane with pores typically between 0.2 to 0.7  $\mu\text{m}$ . For example some pore-  
234 throat sizes in Permo-Triassic sandstones have been determined to be as low as 0.01  $\mu\text{m}$  <sup>43</sup>.  
235 Additionally, deeper groundwaters often have longer residence times <sup>44</sup>. This is implied by a  
236 positive relationship between the mineral weathering product Si and sample depth ( $p < 2 \times$   
237  $10^{-06}$ ). We found a negative correlation between groundwater DOC and Si, with DOC  
238 decreasing by  $6.3 \pm 1.3\%$  with every 10  $\text{mg L}^{-1}$  increase in Si. This relationship has also  
239 been observed in surface waters in the U.S. <sup>45</sup>. The main source of dissolved Si is silicate  
240 mineral dissolution <sup>37</sup>. The negative relationship between DOC and Si is explained by the  
241 dissolved solids accumulated due to water-rock interaction in older groundwaters <sup>46</sup>. In  
242 surface waters, lakes and streams with short water residence times have also been shown  
243 to be biogeochemical hotspots where DOC is rapidly produced and consumed <sup>47</sup>. These  
244 deeper and older groundwaters are more likely to be depleted in DOC due to oxidation  
245 processes, biodegradation and adsorption to soil and aquifer mineral surfaces <sup>48</sup>.

246

## 247 **Land use**

248 There is a significant increase of 19% in groundwater DOC concentrations in urban areas  
249 compared to natural land. Urban land use contributes DOC to groundwater through leaking

250 sewage systems, landfill leaching, animal waste, fertilizer run-off and industrial and  
251 residential waste washed into stormwater drains <sup>27, 49, 50, 51</sup>. Within natural and agricultural  
252 areas there is a significant decrease in median groundwater DOC concentrations where the  
253 subsoil clay fraction is > 30% (n = 2,127) compared to subsoils with clay fraction ≤ 30% (n =  
254 2,372, Fig. S4). In contrast, low (< 1%, n = 4,382) and high (> 1%, n = 106) soil organic  
255 carbon content within natural and agricultural areas do not appear to influence groundwater  
256 DOC concentrations (p = 0.472, Fig. S4) suggesting that adsorption in interlamellar spaces  
257 or complexation with Fe<sup>52</sup> may play a more important role in determining groundwater DOC  
258 concentrations than overlying soil organic carbon content. Our global dataset supports local  
259 scale observations showing that urban land use increases DOC in surface and groundwaters  
260 <sup>53, 54, 55</sup> and shows that the impact of urban land use also extends to groundwater systems on  
261 a broader scale. We found no significant difference (p = 0.841) in groundwater DOC  
262 concentrations between natural and agricultural areas. It is noted that the finding of  
263 increased DOC in urban areas from our space-for-time analysis, as well as a previous  
264 space-for-time analysis <sup>55</sup>, cannot be used to infer how this increase has occurred over time.  
265 A search for available groundwater TOC and DOC timeseries data in urban areas produced  
266 two datasets from Florida, U.S., and Perth, Australia. These data, collected from the 1980's  
267 to present in largely-residential urban areas, show no clear trend in groundwater DOC  
268 concentration (Fig. S5) over this timescale. Longer groundwater DOC timeseries could help  
269 elucidate processes occurring. For example, fluvial DOC concentrations in the Thames  
270 Basin since 1883 <sup>56</sup> have attributed increases in DOC concentrations since World War 2 to  
271 sewerage inputs and changes in land management. We suggest that further groundwater  
272 DOC research is required to investigate the impact of urban area expansion, for example  
273 into lowland regions where DOC might be high, mobilization of previously stable soil DOC as  
274 a result of development, and legacy contamination of groundwater in urban areas.

275

## 276 **Implications**

277 Continental-scale changes to groundwater DOC concentrations respond to changing  
278 temperature and precipitation patterns. Using our results and IPCC<sub>5</sub> (CMIP<sub>5</sub>) climate  
279 projections ([www.worldclim.org](http://www.worldclim.org)), we identify more extreme groundwater DOC concentration  
280 changes associated with changing temperatures modulated by changing precipitation rates  
281 and patterns (Fig. 4). We identify hotspots of high groundwater DOC concentration  
282 (increases of up to 45%) associated largely with increased temperatures in the wettest  
283 quarter of the year in a number of south eastern U.S. states under the “business-as-usual”  
284 Intergovernmental Panel on Climate Change (IPCC) climate change prediction scenario  
285 RCP8.5 (Fig. 4). Increasing temperatures stimulate phenol oxidase activity<sup>57</sup>, which  
286 increases surface water DOC by 5.4% per year in the United Kingdom<sup>58</sup>. Importantly,  
287 relatively recalcitrant phenolic compounds<sup>59</sup> are selectively released as a result of this  
288 process. Therefore, under warmer conditions, more DOC may persist along a flow path and  
289 ultimately enter groundwater systems. This increased carbon loading in groundwaters can  
290 change redox conditions and terminal electron acceptor availability for microorganism use.  
291 This could drive changes in groundwater microbial communities<sup>60</sup> and potentially enhance  
292 survival rates for microbial communities in groundwater systems.

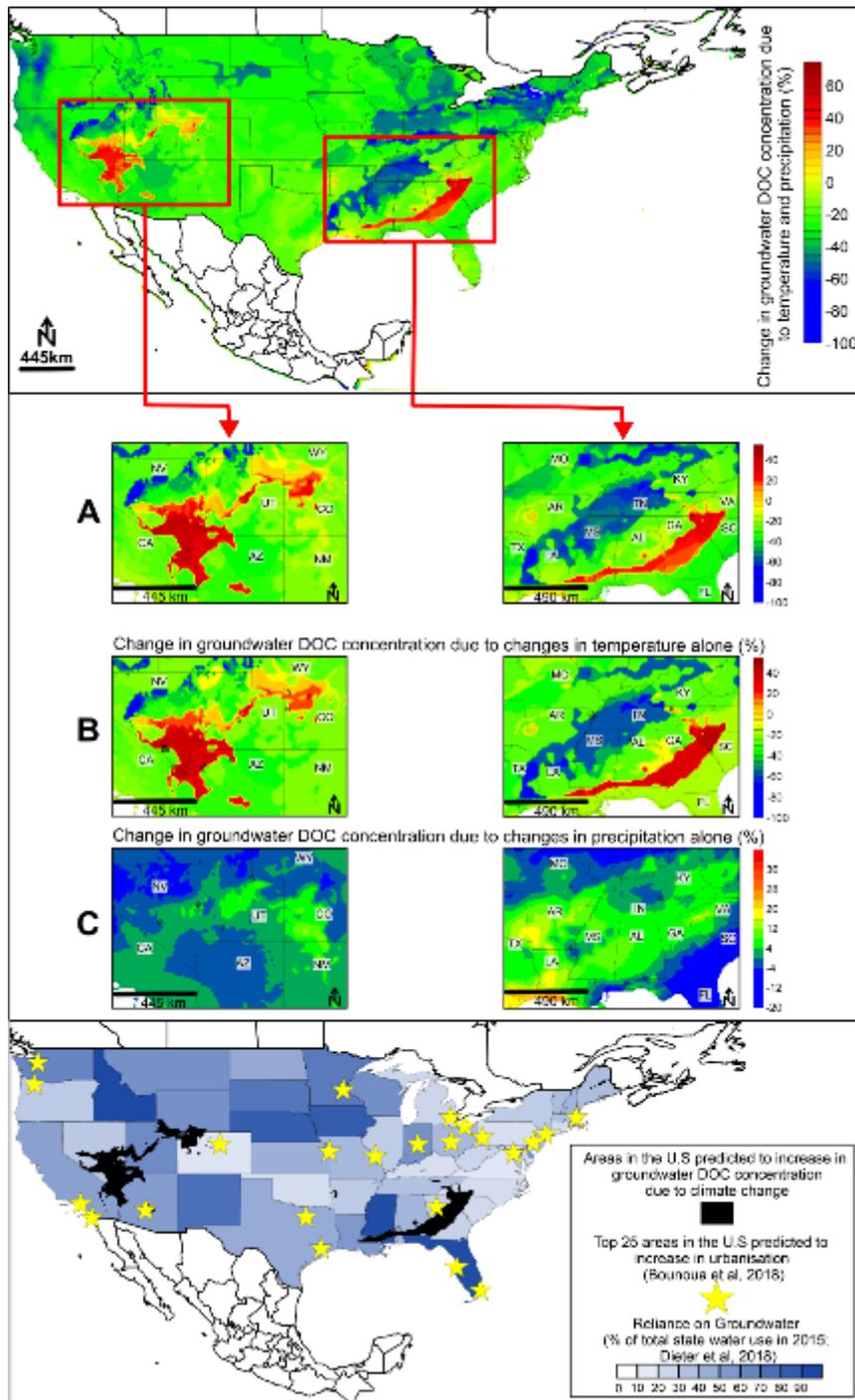
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294 The areas most at risk of future groundwater DOC concentration increases are those facing  
295 increased DOC due to climate change and where urbanization is predicted to occur. It is  
296 likely that DOC leaching will increase due to urbanization and population pressure on waste  
297 disposal networks. This will be a particularly significant issue for regions which have a large  
298 or increasing reliance on groundwater as a source of fresh water. For example areas in the  
299 U.S. predicted to be impacted by DOC increases associated with climate have between 13%  
300 to 87% reliance on groundwater as their source of fresh water (Fig. 4). Some of those  
301 regions were also projected to experience large increases in urbanization by 2020<sup>61</sup>. Our  
302 analysis suggest that this could lead to increased groundwater DOC concentrations,  
303 however it is noted that these results are based on a space-for-time analysis.

304

305 On a global scale, 54% of the worlds' population live in urban areas. By 2050 the world's  
306 urban population will increase to 66% <sup>62</sup>. By 2030, urban area is predicted to increase by 1.2  
307 million km<sup>2</sup> <sup>63</sup>. This presents a significant issue when combined with the current lack of  
308 adequate sanitation services <sup>64</sup> which result in the pollution of groundwater systems. Areas  
309 likely to see urban expansion and population growth include eastern China, India and parts  
310 of Africa <sup>63</sup>. These areas are already facing high urban growth, high rates of the population  
311 without even basic sanitation levels (25% and 56% and up to 64% respectively) <sup>64</sup>, and  
312 severe groundwater contamination issues that threaten local livelihoods <sup>65, 66</sup>. Groundwater  
313 quality issues in south-eastern China may be further compounded by groundwater DOC  
314 increases associated with large predicted increases in temperature (up to 10 °C) in the  
315 wettest quarter of the year by 2050 <sup>30</sup>.

316



317

318 **Fig. 4.** Changes in groundwater DOC concentrations by year 2050 in the U.S. due to  
 319 temperature and precipitation changes. Panel A shows the two areas in the U.S. predicted to  
 320 experience the largest increases in DOC concentration due to temperature and precipitation  
 321 changes by 2050. Panels B and C show changes in DOC concentrations in these areas  
 322 caused by temperature variables (temperature in the wettest and warmest quarters of the  
 323 year) and precipitation variables (precipitation in the wettest and driest months of the year)

324 alone. Groundwater DOC concentrations changes are calculated using model results and  
325 IPCC<sub>5</sub> (CMIP<sub>5</sub>) climate projections from the end of the 20<sup>th</sup> century (average of values from  
326 the period 1960 – 1990) to year 2050 (average of predicted values for the period 2041 –  
327 2060)<sup>30</sup> for a “business-as-usual” climate change scenario (RCP8.5) as outlined in IPCC<sup>67</sup>.  
328 Lowermost map shows U.S. state reliance on groundwater as for total water use<sup>68</sup> overlain  
329 with areas predicted to experience increases in groundwater DOC concentrations due to  
330 climate change variables and urbanization.

331

332 In some locations, increased groundwater DOC concentrations associated with climate  
333 change and urban land cover will lead to an increase in the scale and hence capital and  
334 operational costs of water treatment facilities for groundwater DOC removal. Besides the  
335 direct implications of increased DOC, groundwater organic matter degradation in Holocene  
336 and Pleistocene aquifers in countries including Vietnam and Bangladesh have also been  
337 shown to correlate with an increase in Fe, NH<sub>4</sub> and As due to reductive dissolution of Fe-  
338 oxides in sediments where As is associated with Fe-oxides<sup>3,69</sup>. An increase in these  
339 dissolved species reduces groundwater quality and affects human health.

340

341 One common method of DOC removal from drinking water is via adsorption onto granular  
342 activated carbon. Increasing groundwater DOC concentrations in certain locations will  
343 increase the need for water treatment facilities to implement granular activated carbon as a  
344 second stage filter for DOC removal. The current cost of water for a family of four is  
345 approximately US\$845 per year<sup>70</sup>. The implementation of granular activated carbon filtration  
346 methods by a 6.6 mega gallon per day facility (approximately 25 mega liter per day) would  
347 increase monthly water costs for a family of four by US\$134 per year. This equates to a 16%  
348 increase in annual household water costs in areas of Nevada, Georgia and South Carolina.

349

350 Overall, our investigation reveals that changes in climate and urban land cover are likely to  
351 impact groundwater DOC concentrations globally. These impacts on groundwater DOC will

352 not be evenly distributed. Increases in temperatures in the warmest quarter of the year will  
353 decrease groundwater DOC concentrations due to aridity, whilst increased temperatures in  
354 the wettest quarter of the year will increase groundwater DOC concentrations due to the  
355 stimulation of microbial activity. We identify hotspots of high groundwater DOC  
356 concentrations in areas that will undergo future urbanization and population growth. This  
357 could substantially increase the treatment costs to DOC from groundwater in many locations.  
358 Our results indicate that climate change and urban land cover will not only impact the  
359 quantity of the groundwater resource <sup>23</sup>, but can also decrease groundwater quality and  
360 increase water treatment costs.

361

## 362 **Methods**

### 363 **Literature survey and spatial coverage**

364 Google Scholar, Scopus as well as public data sources were searched using terms “DOM”,  
365 “DOC”, “dissolved organic carbon”, “dissolved organic matter”, “groundwater quality” for  
366 datasets presenting original (i.e. non-summarized) values of DOC. A number of authors,  
367 government departments and colleagues also provided original published and unpublished  
368 datasets. A total of 7,849 unique groundwater DOC observations were obtained from  
369 published and unpublished datasets (Table S1) after eliminating samples with a negative  
370 concentration value (n = 36), or those flagged with a “V” in the National Water Quality  
371 Assessment (NWQA) data (n = 461). The authors were advised that samples flagged with a  
372 “V” were suspected of being contaminated by methanol used in cleaning of the sampling  
373 apparatus and therefore they were excluded from the analysis. The data represents DOC  
374 concentrations for 31 countries on six continents with samples measured between 1992 and  
375 2018. The authors excluded datasets reported to have been sampled from aquifers known to  
376 be heavily contaminated. A large proportion of the data come from samples obtained in U.S.  
377 (n = 5,704), followed by Australia (n = 780), Scotland (n = 270), England and Wales (n =  
378 113), Zambia (n = 110) and Czech Republic (n = 104), with a lesser proportion of samples  
379 obtained from Malawi (n = 89), India (n = 79), Uganda (n = 71), Canada (n = 52), Ethiopia (n

380 = 44), Nepal (n = 40), Poland (n = 40), Kenya (n = 36), Nigeria (n = 35), China (n = 34),  
381 Brazil (n = 30), Portugal (n = 28), Iceland (n = 24), Senegal (n = 22), Denmark (n = 20),  
382 Estonia (n = 19), Belgium (n = 18), Cook Island (n = 17), Argentina (n = 15), Bangladesh (n  
383 = 13), Mali (n = 12), Spain (n = 10), Malta (n = 8), France (n = 7) and Algeria (n = 5). We  
384 used these data to determine average DOC concentrations globally. 5,459 samples from the  
385 U.S. dataset which represent the data collected by the National Water Quality Assessment  
386 (NAWQA) program of the U.S. Geological Survey (USGS) <sup>29</sup>, were then used to generate the  
387 linear mixed model. This dataset was selected due to its large number of samples, ancillary  
388 data (inorganic water quality parameters) and availability of coordinates which allowed for  
389 the extraction of climatic, land use and unsaturated zone thickness data.

390

#### 391 **Global groundwater DOC distributions**

392 DOC concentrations for each country were collected from the sources shown in Table S1.  
393 Non-parametric unpaired one tailed Wilcoxon tests were used to identify differences in the  
394 groundwater DOC concentrations between continents, aquifer types and recharge rates  
395 using the function `wilcox.test()` in RStudio.

396

#### 397 **Worldclim climate data**

398 High resolution (30 arc second) global ESRI grids were obtained for bioclimatic variables  
399 from [www.worldclim.org](http://www.worldclim.org) (v1.4) <sup>30</sup>. Bioclimatic variables including annual mean temperature  
400 and precipitation, mean temperature and precipitation of the driest and wettest quarters,  
401 mean temperature and precipitation of the warmest and coldest quarters, as well as annual  
402 temperature range, isothermality, temperature and precipitation seasonality were extracted  
403 to each sample location using ArcGIS (v10.4.1). Where Worldclim data output showed that  
404 data was unavailable, as indicated by a -999.9 or -9999 value, these were removed and left  
405 blank.

406

#### 407 **Land use data**

408 Land use data was obtained for the U.S. dataset using a shapefile developed by the  
409 University of Maryland, Department of Geography and NASA<sup>32, 33</sup>. Land uses were  
410 assigned to each sample location coordinate using ArcMAP (v10.4.1). Nineteen land use  
411 classifications are used in the file. Land use classifications were reassigned to “agricultural”  
412 (n = 3047) where the land use type included the word “cropland”. Areas were assigned as  
413 “urban” (n = 956) for any area listed as “urban/built up”. Areas were assigned as “wilderness”  
414 (n = 257) for any samples containing the keywords “forest”, “shrublands”, “wetlands”,  
415 “marsh”, “water” and “savannahs”.

416

#### 417 **Unsaturated zone thickness data**

418 Unsaturated zone thickness data<sup>31</sup> and was downloaded through GLOWASIS, the  
419 European Union collaborative project of Global Water Scarcity Information Service, at  
420 [https://glowasis.deltares.nl/thredds/catalog/opendap/opendap/Equilibrium\\_Water\\_Table/cata](https://glowasis.deltares.nl/thredds/catalog/opendap/opendap/Equilibrium_Water_Table/catalog.html)  
421 [log.html](https://glowasis.deltares.nl/thredds/catalog/opendap/opendap/Equilibrium_Water_Table/catalog.html). Data was extracted to each sample location using ArcGIS (v10.4.1).

422

#### 423 **Model development and statistics for U.S. dataset**

424 A mixed linear model was developed using climatic data, land use data and unsaturated  
425 zone thickness data as well as parameters available in the U.S dataset available at  
426 <https://doi.org/10.1594/PANGAEA.896953>. Parameters included DOC, dissolved oxygen  
427 (DO), dissolved iron (Fe), sulphate (SO<sub>4</sub>), magnesium (Mg), manganese (Mn), calcium (Ca),  
428 potassium (K), silica (Si), sodium (Na), fluoride (F), chloride (Cl), pH, sample temperature,  
429 sample depth below land surface, depth to the water table, land elevation, northing,  
430 precipitation in the wettest, driest, coldest and warmest quarters, maximum temperature in  
431 the warmest month, minimum temperature in the coldest month, temperature in the wettest,  
432 driest, coldest and warmest quarters of the year, mean diurnal temperature range,  
433 temperature seasonality, annual temperature range, annual precipitation, precipitation  
434 seasonality, annual average temperature, precipitation in the driest month, aquifer age, and  
435 land use type. Aquifer age was selected as a random effect, with all other variables applied

436 as fixed effects which were selected using the manual Akaike Information Criteria (AIC)  
437 based backward selection using the drop1() function in RStudio. This function allows for the  
438 identification of the variable with the lowest AICs so that they can be removed from the  
439 model.

440

#### 441 **Quality assurance procedures**

442 Prior to data analysis, the data set was screened for “<X” values, which indicate a limit of  
443 detection in the analysis. Where these were identified, the value was replaced with a  
444 randomized value between 0 and X to ensure that bias associated with assigning these data  
445 points as either 0 or 1/2X is eliminated. A number of data points were flagged as potentially  
446 being contaminated with methanol and these samples were removed from the dataset.

447

448 Accuracy of sample coordinates were checked by adding an XY map of sample coordinates  
449 to a world map using Golden Software Surfer® (v 13.6.618). Any samples that were not  
450 located in the correct area as indicated by their ID label was investigated for typological error  
451 in the assigned coordinate and corrected (n = 3).

452

453 Prior to model generation, the response variable “DOC” was log transformed to normalize  
454 the data. Any sample with a missing value for one of the variables was removed using the  
455 na.omit function in R (v 3.3.1). This resulted in a final n of 2,916 complete sample points  
456 used in the model. Predictor variables were then individually fitted to a simple linear model  
457 with DOC as the response variable to check assumptions. Standardized residuals versus  
458 fitted value plots (Fig. S6), Q-Q plots (Fig. S7) and boxplots of residuals (Fig. S8) were  
459 examined for each quantitative model variable to check that the assumption of constant  
460 variance and normality held true for residuals. Collinearity was checked through a regression  
461 matrix using R (v 3.3.1), which confirmed the presence of multicollinearity between some  
462 variables. The variance inflation factors (VIFs) for each variable were also checked.  
463 Typically, a variable is considered collinear with another variable when the VIF is greater

464 than 10<sup>71</sup>. Some literature however recommends removing variables with VIFs greater than  
465 4 or 5<sup>72</sup>. Some variables were known to covary, and thus were removed from the list of  
466 variables. These including Mn (due to covariance with Fe), EC (due to covariance with ions),  
467 temperature in the coldest and warmest months (covariance with temperatures in the coldest  
468 and warmest quarters), temperature and precipitation seasonality (due to covariance with  
469 temperature and precipitation range). All remaining variables with VIFs greater than 4 were  
470 then removed, with the variable with the highest VIF removed first before re-running the  
471 code each time until all remaining variables had VIFs > 10. The variables with VIFs > 10  
472 were removed in the following order; annual temperature, temperature in the coldest quarter,  
473 precipitation in the driest quarter, annual precipitation, isothermality, precipitation in the  
474 wettest quarter, precipitation in the warmest quarter, precipitation in the coldest quarter,  
475 chloride, temperature in the driest quarter, northing, mean diurnal range. The results are  
476 reported as a percent change in DOC concentration, with standard error reported where  
477 possible (i.e. for continuous fixed effects variables).

478

#### 479 **Change in groundwater DOC concentration due to climate change in 2050**

480 Contours for changes in groundwater DOC concentration due to climate change in 2050  
481 were developed by using current climate grid files from Worldclim v1.4<sup>30</sup> and future IPCC<sub>5</sub>  
482 (CMIP<sub>5</sub>) climate projections ([www.worldclim.org](http://www.worldclim.org)). Current climate values for climate  
483 variables used in the model (temperature in the wettest quarter of the year, temperature in  
484 the warmest quarter of the year, precipitation in the wettest month of the year and  
485 precipitation in the driest month of the year) were subtracted from future IPCC<sub>5</sub> (CMIP<sub>5</sub>)  
486 climate projection values ([www.worldclim.org](http://www.worldclim.org)) for the same variables for the year 2050 under  
487 a “business-as-usual” representative concentration pathway (RCP8.5) using Surfer®  
488 v.11.0.642. As DOC units in the model are log natural concentration values, the difference  
489 from zero for the exponents of the intercepts for the four variables were multiplied by the  
490 difference in current and future values using a positive or negative sign at the front of the  
491 exponent depending upon whether the variable was positively or negatively correlated with

492 DOC concentration. This provides a percent change in groundwater DOC concentration due  
493 to change in each climate variable predicted for 2050. The four grid files containing change  
494 in DOC concentration associated with each of the four variables were then added together  
495 into a single grid file to get a total change in DOC (%) associated with climate change in  
496 2050.

497

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538

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542 Extended Data - Tables supporting document. Unpublished datasets that support the  
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