

Supplementary Table 1. Average copper, ligand and speciation data across all stations for each month sampled, with range beneath in italics. Sal: salinity; Cu_d: dissolved copper, HS_{Cu}: copper-binding humics; thiols (nM thiourea equivalent), L₁, L₂, log K'_{CuL1} and K'_{CuL2}, the calculated concentration of free Cu²⁺ and the percentage of copper bound as CuL₁ and CuL₂. CuL₁ was found to correspond with thiol-bound copper at most stations and therefore occurs primarily as monovalent copper (Cu(I)); CuL₂ is predominantly copper bound to humic substances therefore occurs as divalent copper (Cu(II)).

Month	Salinity	T	Cu_d	HS_{Cu}	Thiol	L₁	Log K'_{CuL1}	L₂	Log K'_{CuL2}	Cu²⁺	Cu as CuL₁	Cu as CuL₂
(mean)		(°C)	(nM)	(mg/L)	(nM)	(nM)		(nM)		(fM)	%	%
Apr	15.8	20.1	25.1	3.83	47.6	36.3	14.3	69.5	12.8	3.8	89	11
<i>Range</i>	<i>13.2 – 17.4</i>	<i>19.1 – 20.6</i>	<i>7.1 – 65</i>	<i>2.6 – 5.5</i>	<i>31 – 74</i>	<i>21.0 – 50</i>	<i>14.0 – 14.8</i>	<i>57 – 96</i>	<i>12.4 – 13.1</i>	<i>2.0 – 7.5</i>	<i>82 - 97</i>	<i>3 - 18</i>
May	19.8	24.9	11.1	4.13	32.4	32.0	14.2	73.2	12.6	3.4	91	9
	<i>18.2 – 22.4</i>	<i>18.2 – 22.4</i>	<i>6.4 – 16.5</i>	<i>2.3 – 6.3</i>	<i>18 – 41</i>	<i>18 – 41</i>	<i>14.1 – 14.3</i>	<i>39 – 112</i>	<i>12.5 – 12.7</i>	<i>1.1 – 5.2</i>	<i>82 - 96</i>	<i>4 - 18</i>
June	21.8	28.8	8.7	3.61	53.3	42.1	14.6	63.0	12.2	0.7	99	1
	<i>21.4 – 22.4</i>	<i>21.4 – 22.4</i>	<i>7.7 – 10.4</i>	<i>2.6 – 5.4</i>	<i>39 – 68</i>	<i>39 – 68</i>	<i>14.4 – 14.7</i>	<i>51 – 80</i>	<i>12.1 – 12.3</i>	<i>0.4 – 0.8</i>	-	-
July	26.0	30.4	6.7	2.22	34.4	23.0	14.8	39.2	12.5	1.0	98	2
	<i>25.0 – 27.2</i>	<i>25 – 27.2</i>	<i>4.4 – 9.1</i>	<i>1.9 – 2.5</i>	<i>16 – 62</i>	<i>16 – 62</i>	<i>14.6 – 14.9</i>	<i>33 – 44</i>	<i>12.2 – 12.8</i>	<i>0.3 – 1.8</i>	<i>94 - 99</i>	<i>1-6</i>

Aug	26.0	30.4	6.7	2.97	32.0	30.3	14.9	63.4	13.0	0.4	96	4
	<i>24.7 – 27.1</i>	<i>24.7 – 27.1</i>	<i>4.7 – 9.5</i>	<i>2.3 – 3.9</i>	<i>24 – 38</i>	<i>24 – 38</i>	<i>14.7 – 15.2</i>	<i>45 – 82</i>	<i>12.9 – 13.0</i>	<i>0.2 – 0.5</i>	<i>93 - 97</i>	<i>3-7</i>
Sept	29.5	29.1	6.2	2.23	26.9	25.7	14.6	48.1	13.1	0.7	91	9
	<i>28.9 – 29.9</i>	<i>29.2 – 29.9</i>	<i>3.6 – 9.6</i>	<i>1.9 – 2.6</i>	<i>26 – 32</i>	<i>21 – 32</i>	<i>14.2 – 14.9</i>	<i>39 – 56</i>	<i>12.9 – 13.3</i>	<i>0.5 – 0.9</i>	<i>84 - 98</i>	<i>2 - 16</i>
Oct	27.8	26.6	4.5	2.25	29.0	22.5	14.4	38.9	13.3	0.8	87	13
	<i>27.0 – 28.1</i>	<i>27 – 28.1</i>	<i>2.9 – 6.1</i>	<i>2.1 – 2.4</i>	<i>20 – 39</i>	<i>20 – 39</i>	<i>14.2 – 14.6</i>	<i>30 – 48</i>	<i>13.2 – 13.4</i>	<i>0.6 – 0.9</i>	<i>85 - 89</i>	<i>11 – 15</i>
Dec	27.9	14.4	8.0	1.90	30.1	27.0	14.3	42.9	12.8	2.1	92	8
	<i>7.6 – 28.0</i>	<i>27.6 - 28</i>	<i>5.8 – 10.2</i>	<i>0.4 – 2.8</i>	<i>23 – 44</i>	<i>23 – 44</i>	<i>14.1 – 14.5</i>	<i>30 – 54</i>	<i>12.5 – 13.2</i>	<i>1.2 – 3.5</i>	<i>85 - 98</i>	<i>2 - 15</i>