

Surface Water Samples – Containers, Preservation, Hold Times Table  
 NCDWR-Water Sciences Section-Chemistry Laboratory

<b>Surface Water Samples: Containers, Preservation and Hold Times Table</b>				
<b>North Carolina Division of Water Resources, Water Sciences Section – Chemistry Laboratory</b>				
<b>Reference: 40 CFR Part 136.3 Table II</b>				
<p>Listed below is information on the collection and preservation of surface water samples. The amount of sample listed is for average conditions; therefore, if you suspect that unusual conditions or interferences exist, please submit double the amount of sample.</p> <ul style="list-style-type: none"> <li>• <b>Excluding volatile organics and sulfide</b>, a one-half inch air space should be left in all containers to allow for mixing before analysis.</li> <li>• <b>When submitting a filtered sample, write "DIS" (for dissolved) in the box beside the parameter(s) on the field sheet.</b></li> </ul>				
<b>Samples must be shipped to the Laboratory as soon as possible after collection.</b>				
Parameter <sup>1</sup>	Minimum Required Volume	Container <sup>13</sup> P-Plastic G-Glass	Preservation <sup>20</sup>	Maximum Holding Time <sup>21</sup>
<b>Microbiology Unit Parameters:</b>				
Acidity	200 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	14 days
Alkalinity •includes bicarbonate & carbonate	200 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	14 days
BOD, 5-day	1 liter	P	Cool ≤ 6°C <sup>24</sup>	48 hours <sup>2</sup> <i>(notify lab)</i>
CBOD, 5-Day	1 liter	P	Cool ≤ 6°C <sup>24</sup>	48 hours <sup>2</sup> <i>(notify lab)</i>
Coliform: Fecal, Total, <i>E. coli</i> and Enterococci	250 ml ( <b>each</b> ) <i>(cannot be combined)</i>	P <sup>3</sup> (sterile)	Cool <10°C 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1ml 10% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /125 ml) & 15% EDTA <sup>3</sup>	6 hours <sup>4</sup>
Specific Conductance	200 ml	P (disposable)	Cool ≤6°C <sup>24</sup>	28 days
TOC	500 ml	P (disposable)	H <sub>3</sub> PO <sub>4</sub> to pH<2; Cool ≤ 6°C <sup>24</sup>	28 days

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Parameter <sup>1</sup>	Minimum Required Volume	Container <sup>13</sup> P- Plastic G- Glass	Preservation <sup>20</sup>	Maximum Holding Time <sup>21</sup>
DOC	500 ml <i>Include a Field Blank with DOC samples</i>	P (disposable)	Field filter using 0.45um pore size; H <sub>3</sub> PO <sub>4</sub> to pH<2 Cool ≤ 6°C <sup>24</sup>	28 days
Turbidity	200 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	48 hours <sup>2</sup>
<b>Wet Chemistry Unit Parameters:</b>				
Bromide	500 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	28 days
Chloride				
Fluoride				
Sulfate				
Chlorophyll <i>a</i> <sup>10</sup>	500 ml	P (Brown wide-mouth)	Cool ≤ 6°C <sup>24</sup> <i>-if filtered in field, store filters in the dark; if not delivered to lab within 24 hours, store frozen.</i>	Filter within 24 hours <sup>23</sup> <i>(21 days after filtration)</i>
Color: ADMI	400 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	48 hours <sup>2</sup>
Color: Platinum Cobalt	400 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	48 hours <sup>2</sup>
COD	200 ml	P (disposable)	25% H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool ≤ 6°C <sup>24</sup>	28 days
Cyanide, Total <sup>27</sup>	2 liters (2 x 1-liter bottles)	P	6N NaOH to pH >10, not exceeding a pH of 11; Cool ≤ 6°C <sup>24</sup> <i>Add 0.6 g ascorbic per bottle if chlorine present (see footnote 6)</i>	14 days <i>(24 hours if chlorine present and treated with ascorbic acid)</i>
Formaldehyde	500 ml	P (disposable)	Cool ≤ 6°C <sup>24</sup>	NA

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Parameter <sup>1</sup>	Minimum Required Volume	Container <sup>13</sup> P- Plastic G- Glass	Preservation <sup>20</sup>	Maximum Holding Time <sup>21</sup>
Hexavalent Chromium	400 ml <i>Recommend field blank</i>	P (disposable)	Field filter using 0.45-um pore size followed by: Adjust pH to 9.3 – 9.7 using sample adjustment buffer <sup>28</sup> Cool $\leq 6^{\circ}\text{C}^{24}$	28 days
MBAS	500 ml	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{24}$	48 hours <sup>2</sup> <i>(notify lab)</i>
Microcystin	200 ml	PETG	Cool $\leq 6^{\circ}\text{C}^{24}$	14 days
Oil & Grease, HEM	2 liters (2 x 1-liter bottles) <sup>17</sup>	G (wide-mouth quart jar w/ Teflon-lined cap)	1:1 H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool $\leq 6^{\circ}\text{C}^{24}$	28 days
Phenols, Total recoverable	2 liters (2 x 1-liter bottles)	G <i>(Phenol bottle only)</i>	1:1 H <sub>2</sub> SO <sub>4</sub> to pH < 2 Cool $\leq 6^{\circ}\text{C}^{24}$ <i>(1 ml of Ferrous Ammonium Sulfate if sample contains oxidizer-prior to acid)</i>	28 days
Residue, Non-Filterable <i>-Total Suspended Solids</i> (plus Volatile/Fixed, if requested)	500 ml <sup>25</sup>	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{24}$	7 days
Residue, Total <i>-Total Solids</i> (plus Volatile/Fixed, if requested)	500 ml <sup>25</sup>	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{24}$	7 days
Residue, Filterable <i>-Total Dissolved Solids</i>	500 ml <sup>25</sup>	P (disposable)	Cool $\leq 6^{\circ}\text{C}^{24}$	7 days

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Sulfide	120 ml (40-ml x 3) <sup>9</sup>	G 40-ml VOA vials with Teflon-lined septum	Add 1 ml of 2N zinc acetate plus 6 N NaOH to pH>9; Cool ≤6°C <sup>24</sup> <i>Leave no headspace in bottle.</i>	7 days
Tannin and Lignin	500 ml	P (disposable)	Cool ≤6°C <sup>24</sup>	28 days
<b>Parameter<sup>1</sup></b>	<b>Minimum Required Volume</b>	<b>Container<sup>13</sup></b> <b>P – Plastic</b> <b>G - Glass</b>	<b>Preservation<sup>20</sup></b>	<b>Maximum Holding Time<sup>21</sup></b>
<b>Other Parameters:</b>				
pH <sup>(5)</sup>	Lab analysis inappropriate; analyze in field within 15 minutes of sample collection.			
Hardness, Total <i>-request by checking Hardness, Total as CaCO<sub>3</sub>, on field sheet. -or check Ca and Mg (can be part of metals sample) Total Hardness=2.497[Ca mg/L] + 4.118[Mg mg/L] •Non-carbonate hardness = total hardness – total alkalinity</i>	500 ml	P (disposable)	1+1 HNO <sub>3</sub> to pH<2	6 months
<b>Nutrients Unit Parameters:</b>				
Ammonia (NH <sub>3</sub> -N)	500 ml <i>(1 bottle for all, except when chlorine present; then include additional bottle of de-chlorinated sample for NH<sub>3</sub>-N)</i>	P (disposable)	25% H <sub>2</sub> SO <sub>4</sub> to pH<2 <sup>7</sup> Cool ≤6°C <sup>24</sup> <i>0.008% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to de- chlorinate (See note 11)</i>	28 days
Nitrate-Nitrite (NO <sub>3</sub> +NO <sub>2</sub> – N)				
Total Kjeldahl Nitrogen (TKN)				
Total Phosphorus (TP)				
Dissolved Nutrients (4 parameters above)	200 ml (1 bottle)	P (disposable)	Field filter using 0.45um pore size; and then follow preservation above	28 days

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Nitrite (NO <sub>2</sub> - N)	200 ml	P (disposable)	Cool ≤6°C <sup>24</sup>	48 hours <sup>2</sup> <i>(notify lab)</i>
Nitrate (NO <sub>3</sub> -N)	Calculated value using analytical results for NO <sub>3</sub> +NO <sub>2</sub> -N and NO <sub>2</sub> -N; submit samples for NO <sub>3</sub> +NO <sub>2</sub> -N and NO <sub>2</sub> -N			
Orthophosphate (PO <sub>4</sub> -P)	200 ml	P (disposable)	Field filter within 15 minutes using 0.45 um pore size; Cool ≤6°C <sup>24</sup>	48 hours <sup>2</sup> <i>(notify lab)</i>
<b>Parameter<sup>1</sup></b>	<b>Minimum Required Volume</b>	<b>Container<sup>13</sup></b> P – Plastic G - Glass	<b>Preservation<sup>20</sup></b>	<b>Maximum Holding Time<sup>21</sup></b>
<b>Metals Unit Parameters:</b>				
Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr (Total), Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, and Hg <sup>19</sup> .	500 ml  (1 bottle)	P (disposable)	1+1 HNO <sub>3</sub> to pH<2 <sup>26</sup>	6 months  (28 days for Mercury)
Boron	500 ml	P (disposable)	1+1 HNO <sub>3</sub> to pH<2 <sup>26</sup>	6 months
Mercury EPA 1631 E Hg (trace-level total Hg)	500 ml  <i>A Field Blank must accompany each trace-level Hg sample</i>	G (borosilicate), Teflon-lined cap	None required for total and dissolved Mercury.  Use clean sampling techniques as described in EPA Method 1669.	28 days until preservation with BrCl <sup>22</sup> if the sample is oxidized in the sample bottle. Preserved samples are stable for up to 90 days from collection.
<b>Organics Branch Parameters:</b>				
Acid Herbicides	4 liters <sup>8</sup>	G (amber), Teflon-lined cap	Cool ≤6°C <sup>24</sup>  0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1ml 10% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /125 ml) <sup>11</sup>	7 days until extraction <sup>15</sup> <i>40 days after extraction</i>
Pesticides -Organochlorine -Organonitrogen -Organophosphorus	4 liters <sup>8</sup>	G (amber), Teflon-lined cap	Cool ≤6°C <sup>24</sup>  0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1ml 10% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /125 ml) <sup>11</sup>	7 days until extraction <sup>15</sup> <i>40 days after extraction</i>

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PCBs (polychlorinated biphenyls)	4 liters <sup>8</sup> <i>(can be same bottle as for Pesticides)</i>	G (amber), Teflon-lined cap	Cool ≤6°C <sup>24</sup> 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1ml 10% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /125 ml) <sup>11</sup>	7 days until extraction <sup>15</sup> 40 days after extraction
Semi-Volatile Organics (Base/Neutral & Acid Extractables)	4 liters <sup>8</sup>	G (amber), Teflon-lined cap	Cool ≤6°C <sup>24</sup> 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1ml 10% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /125 ml) <sup>11</sup>	7 days until extraction 40 days after extraction
<b>Parameter<sup>1</sup></b>	<b>Minimum Required Volume</b>	<b>Container<sup>13</sup></b> <b>P – Plastic</b> <b>G - Glass</b>	<b>Preservation<sup>20</sup></b>	<b>Maximum Holding Time<sup>21</sup></b>
TPH Diesel Range (aqueous)	4 liters <sup>8</sup>	G (amber), Teflon-lined cap	Cool ≤6°C <sup>24</sup> 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.1ml 10% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> /125 ml) <sup>11</sup>	7 days until extraction 40 days after extraction
Volatile Organics (VOA)	40 ml x 4 <sup>9</sup> <i>A Trip blank (3 vials) must accompany all VOA samples</i>	G  VOA vials, Teflon-lined septum	Cool ≤6°C <sup>24</sup>  0.6g Ascorbic Acid, or 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>11</sup> HCl to pH 2 <sup>14,16</sup>  <i>Leave no headspace in bottle.</i>	14 days  (7 days for aromatics only when unpreserved)
1,4-Dioxane	40 ml x 4 <sup>9</sup> <i>A Trip blank (3 vials) must accompany all samples for 1,4- Dioxane</i>	G  VOA vials, Teflon-lined septum	Cool ≤6°C <sup>24</sup>  0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>11</sup>  <i>Leave no headspace in bottle.</i>	7 days
TPH Gasoline Range (aqueous)	40 ml x 4 <sup>9</sup> <i>A Trip blank (3 vials) must accompany all VOA samples.</i>	G  VOA vials, Teflon-lined septum	Cool ≤6°C <sup>24</sup>  0.6g Ascorbic Acid or 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>11</sup> HCl to pH 2 <sup>14,16</sup>  <i>Leave no headspace in bottle.</i>	14 days

**Key to Footnotes:**

- (1) Parameters grouped together e.g. Nutrients, may be submitted in the same bottle.
- (2) 48 hours is the maximum holding time; however, samples should be submitted to the Lab as soon as possible.
- (3) Use the 250ml wide-mouth sterile plastic bottles for all samples. All bottles contain sodium thiosulfate and EDTA reagents and should not be rinsed prior to sample collection.

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- (4) To be NPDES-compliant, samples for coliform must be delivered to the laboratory within 6 hours of sample collection in order to meet the regulatory 8-hour hold time.
- (5) To be NPDES-compliant, pH analysis must be performed on site.
- (6) Add 0.6 g of ascorbic acid per 1-liter bottle only if sample contains residual chlorine; must be checked and treated for chlorine prior to pH adjustment.
- (7) Caution: Addition of excessive amounts of acid will interfere with the test procedures. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) preservative should be added using a graduated dispensing device, or from an ampule or vial containing pre-measured volume. Although the requirement is for pH<2, the ideal range for Nutrients is a sample pH of 1.5-2.0. For most surface water samples, this pH can be achieved by adding 2.0 ml of 1:3 (25%) H<sub>2</sub>SO<sub>4</sub> solution (or 1.0 ml of 1:1 (50%) H<sub>2</sub>SO<sub>4</sub> solution) to 500 ml of the water sample. Confirm pH using pH test strips.
- (8) In a glass container, submit a small quantity of the pure compound of any suspected material.
- (9) Fill the bottle to overflowing and cap, leaving no air space.
- (10) EPA Method 445.0, Revision 1.2, September 1997; modified filter kit.
- (11) Should only be used in the presence of residual chlorine. Add sodium thiosulfate or ascorbic acid (as specified) to the container first; fill at least half way before adding acid (if used). If residual chlorine is detected in a water sample (generally effluent), then it is recommended that the 500ml water sample for Nutrients be de-chlorinated at the time of sample collection. The recommended de-chlorination reagent for Nutrients is sodium thiosulfate (dissolve 3.5 grams in deionized water, then dilute to 1 liter). One mL of this solution will remove 1mg/L of residual chlorine in a 500mL sample (prior to acid preservation).
- (12) Footnote no longer needed.
- (13) The container types listed are those commonly used throughout the Division. Other container types may be acceptable. Please consult the laboratory about use of proper containers before deviating from those listed. (P-plastic, G-glass, P (disposable)-Plastic Disposable bottle)
- (14) Samples submitted for purgeable halocarbons only should not be acid-preserved.
- (15) Samples submitted for pesticide and acid herbicide analyses must be extracted within 72 hours of collection if the pH is not adjusted in the lab to a pH range of 5-9.
- (16) Samples submitted for purgeable aromatics with no pH adjustment must be analyzed within 7 days of collection.
- (17) The entire contents must be used for analysis.
- (18) Footnote no longer used.
- (19) For dissolved metals, samples should be filtered with a 0.45micron filter immediately on-site before adding preservative.
- (20) Sample preservation should be performed immediately upon collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then the samples may be preserved by maintaining at ≤ 6° C until compositing and sample splitting is completed.
- (21) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Collection times must allow for sample preparation and analytical setup. Some samples may not be stable for the maximum time period given in the table. Collectors are obligated to hold the sample for as short a time as possible especially if knowledge exists showing that this is necessary to maintain sample stability.
- (22) If the samples are oxidized (digested) with bromine chloride (BrCl) in the same bottle that they are collected, then the preservation of the sample may be delayed up to twenty-eight days after the time of sample collection. The total holding time with proper preservation for EPA Method 1631 is ninety days after collection. Reference: EPA Method 1631, Revision E, Section 8.5.
- (23) Samples are cooled to 6° C at the time of collection. Due to the limitations of filtering samples in the field, it is the DWR Water Sciences Section's policy to filter chlorophyll *a* samples the day that the samples are received at the lab, not to exceed 24 hours from collection. Filters can be stored frozen in the dark for as long as 3 and 1/2 weeks without significant loss of chlorophyll *a*.
- (24) Aqueous samples must be preserved ≤ 6° C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification “≤ °C” is used in place of the “4 °C” and “< 4 °C” sample temperature requirements listed in some methods. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).
- (25) Larger sample volumes may need to be submitted to achieve lower PQLs.
- (26) If sample is not field preserved, HNO<sub>3</sub> must be added 24 hours prior to analysis.
- (27) The QAO has a licensed copy of ASTM D7365-09a, which details sampling, preservation and mitigating interferences in water samples for analysis of Cyanide. Consult the Laboratory Quality Assurance Officer for mitigation instructions if any of the following interferences are suspect: sulfide, sulfur, aldehydes, sulfite, thiosulfate, thiocyanate, particulate cyanide, carbonate, nitrate-nitrite.
- (28) For pH adjustment of water samples for hexavalent chromium, use Sample Adjustment Buffer solution provided by laboratory. Add 1 mL of buffer per 100 mL of sample. Confirm pH with narrow-range pH strip or pH meter.