Method DWRL_123TCP: Measurement of low-level 1,2,3-Trichloropropane in Drinking Water by Isotope Dilution Quantitation Purge and Trap Gas Chromatography-Mass Spectrometry

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1.0 Identification of the method

1.1 This method determines 1,2,3-Trichloropropane (1,2,3-TCP), CAS No. 96-18-4 in drinking water at low ng/L (parts-per-trillion, ppt) concentrations by isotope dilution quantitation using purge and trap (P&T) sample introduction coupled with gas chromatography and multiple ion monitoring mode (MIM), electron ionization mass spectrometry (GC-MS). The method is based on SRL524M and designated hereafter as DWRL_123TCP.

2.0 Applicable matrix or matrices

2.1 DWRL_123TCP is applicable to the analysis of drinking water, surface water, and groundwater.

3.0 Limits of detection and quantitation

3.1 Method detection limit (MDL) is the smallest concentration that this method can measure while having 99% confidence that the analyte concentration is greater than zero. The MDL shall be determined following the US EPA method for the determination of MDL, (Reference 23.1). The MDL for 1,2,3-TCP determined with this method complies with the MCL 5 ppt set under CA regulations for this compound (See Appendix I and II).

3.2 The reporting limit (RL) for this method is defined by the laboratory but must be ≤ CA Detection Limit for Reporting (DLR) value of 5 ppt. The RL must be a verified value.

4.0 Scope and application, including analytes to be analyzed

4.1 DWRL_123TCP is designed to identify and quantify 1,2,3-TCP (CAS: 96-18-4) at parts per trillion levels (ppt or ng/L) using isotopic dilution quantitation, purge and trap (P&T) gas chromatography mass spectrometry (GC-MS) in drinking water, surface water, and groundwater samples.

4.2 DWRL_123TCP is based on SRL524M, developed in 2002, by the former Sanitation and Radiation Laboratories Branch, CDPH. Method modifications are described in specific details throughout the method.

4.3 Triple quadrupole or single quadrupole mass spectrometer instrument can be used for this method.

5.0 Summary of the method

5.1 1,2,3-TCP and internal standard (ISTD), deuterated 1,2,3-trichloropropane (1,2,3-TCP-d5) at 40 ppt, are purged from the sample matrix with ultra-high purity helium. Purged sample components are trapped in a K trap (Vocarb 3000®) containing sorbent Carbopack B/Carboxen™ 1000 & 1001 as sorbent materials. Following the purging step, the trap is heated and backflushed with helium to desorb the trapped materials onto a gas chromatography column interfaced to a mass spectrometer detector. With the use of a method-specific temperature program, gas chromatography separates the desorbed mixture. 1,2,3-TCP and 1,2,3-TCP-d5 are determined with multiple ion monitoring (MIM). 1,2,3-TCP is identified using retention time, comparing fragment ions from the samples to calibration standards,

and comparing the ion ratios (See Sections 16.4 - 16.7 for further info). Isotopically labeled 1,2,3-TCP's quantitation ion area is compared to that of 1,2,3-TCP to achieve isotope dilution quantitation.

6.0 Definitions

6.1 Batch of samples: A set of samples analyzed on the same instrument during a 24-hour period, including no more than 20 field Samples. A batch of samples begins and ends with the analysis of the appropriate continuing calibration check (CCC) standards. A sequence of samples can include more than one batch of samples. Laboratory QC samples are not accounted in the 20 samples of a batch, but they are part of a sequence of samples and run within a sequence or within a batch of samples.

6.2 Calibration standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the ISTD. The CAL standards are used to calibrate the instrument response with respect to the analyte concentration.

6.3 Field Duplicates (FD): Two separate samples collected at the same time (sequentially; same time and day), placed under identical circumstances as possible and treated the same throughout field and laboratory procedures. Analyses of field duplicate samples give a measure of the precision associated with sample collection, preservation, and storage in combination with laboratory procedures.

6.4 Internal Standard (ISTD): A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The ISTD must be an analyte that is not a sample component.

6.5 Laboratory Fortified Blank (LFB): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the results of the measurements in the sample batch are accurate.

6.6 Laboratory Fortified Sample Matrix (LFSM): An aliquot of a field sample to which known quantities of the method analytes are added in the laboratory. The LFSM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a FD and the measured values in the LFSM corrected for background concentrations.

6.7 Laboratory Reagent Blank (LRB): An aliquot of laboratory reagent water that is treated exactly like any sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

6.8 Method Detection Limit (MDL): MDL is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

6.9 Primary Dilution Standard solution (PDS): A solution of the analyte prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

6.10 Quality Control Sample (QCS): A solution of the method analyte(s) of known concentration, which is used to fortify an aliquot of LRB. The analyte(s) standard used to make the QCS, must be obtained from a source external to the laboratory and must be different from the source of the calibration standards. When a different commercial source is not available, a different lot # from the same commercial source or a previous quality control sample, purchased from a confirmed certified material provider, can be used to make the QCS. A QCS is used to check laboratory performance with externally prepared test materials.

6.11 Reporting Limit (RL): The concentration that can be reported by a laboratory as a quantitated value for a target analyte in a sample following analysis. This defined and verified concentration must meet the criteria in Section 19 and must not be lower than the concentration of the lowest calibration standard for the analyte.

6.12 Trip Blank (TB): An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The trip blank is NOT requested to be opened in the field. The purpose of the TB is to determine whether contamination occurs during sampling or sample shipping and handling.

7.0 Interferences

7.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. Avoid using Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device. Analysis of LRB samples provide information on contaminants that may be present. Recommended troubleshooting steps for such contamination are changing the purge gas source, baking and/or replacing the purge gas filter/trap.

7.2 Method interferences may occur by contaminants in solvents, reagents and glassware, and other sources of processing samples. It is important that standards are prepared in the same solvent, i.e. the solvent for calibration standards stocks and working solutions be in the same final solvent/reagent used during quality control samples preparation, etc.

7.3 Carryover could be a potential issue after running a highly concentrated sample. At a minimum one LRB should be analyzed following a high concentrated sample to minimize sample cross- contamination. If high concentration samples are anticipated, blanks should be run after each sample.

7.4 A laboratory can run a mixed standard of volatile organic chemicals (VOCs) under the conditions described in this methodology to identify possible interferences (single ion monitoring (SIM) with 2 or 3 ions used for identification and confirmation of 1,2,3-TCP).

8.0 Safety

8.1 1,2,3-TCP is a chlorinated hydrocarbon with high stability in water. It has been used as an industrial solvent and as a cleaning and degreasing agent. It is a persistent pollutant in groundwater and has been classified as “likely to be carcinogenic to humans” by the U.S. EPA (Reference 23.5). Any exposure to the chemical, especially concentrated standards, should be minimized. Before beginning this procedure, read the Safety Data Sheet.

9.0 Equipment and supplies

9.1 Any substitution of equipment supplies and/or consumables from the suggested materials in this method are permitted but must be shown to meet the method requirements. Catalog numbers are included for illustration only.

9.2 Purge and Trap (P&T) coupled with GC-MS system

9.2.1 Autosampler:

9.2.1.1 EST Analytical Centurion (model: CENTW645061218)

9.2.1.2 Loop, 25 mL sample, (EST Analytical, CENTW (water only), Product ID: A011634015)

9.2.1.3 For 5 mL sample volume, Loop, 5 mL, W & WS (common 5ml loop), (EST Analytical, Part number: A011634011)

9.2.2 P&T Concentrator:

9.2.2.1 EST Analytical Encon Evolution (model: EV950041018) or Teledyne Tekmar Atomx XYZ (model:ASX-7200HR)

9.2.2.2 Sparge Tube 25 mL Fritted (EST Analytical, part number: E70100-25ML)

9.2.2.3 K Trap, Vocarb-3000 (EST Analytical, part number: E70300-K03)

9.2.2.4 Carbopack B/Carboxen™ 1000 & 1001 as sorbent material (Sigma Aldrich, part number: E70300-K03)

9.2.2.5 For 5 mL sample volume, Sparge Tube 5 mL Fritted (EST Analytical, part number: E70100- 5ML)

9.2.3 Gas Chromatography System:

9.2.3.1 Thermo Scientific model Trace 1310 or Agilent Model 8890

9.2.3.2 Capillary column: Factor Four DB-624, 20 m x 0.18 mm, 1.0 µm film or equivalent

9.2.3.3 Carrier gas: helium, ultra-high purity, 99.999%

9.2.3.4 Gas filter: Thermo Scientific™ Super Clean™ Gas Cartridge Filters, Fisher scientific, part number: 60180825

9.2.3.5 Kiner: Thermo Scientific™ LinerGOLD™ GC Liners: Fisher Scientific part number: 03-151- 668 or equivalent

9.2.4 Mass spectrometry (MS) System for each instrument:

9.2.4.1 MS Thermo Fisher TSQ 8000Duo, with TSQ Duo MS Workstation and software Chromeleon™ 7 and NIST/EPA/NIH MS library

9.2.4.2 Agilent 5977B MSD and software MassHunter™ version 10.0

9.3 Hot plate (for boiling water)

9.4 Sample collection bottles: 40 mL volatile organic compound analysis (VOA) vials, amber glass, with PTFE-lined silicon septum cap, pre-cleaned to EPA level 2 specifications: Thermo Scientific™ I- Chem™ Amber VOA Glass Vials with 0.125 in. Septa/ Thermo Scientific™ 14140A/DB, Fisher Scientific part number: 12-100-105 or equivalent

9.5 A pH meter or pH 0-6 color indicator strips (ColorpHast, EM Science, part number 9586)

9.6 Volumetric flasks (Grade A), 10, and 100, mL, cleaned as follows:

9.6.1 Wash with detergent and water

9.6.2 Rinse with deionized/demineralized water

9.6.3 Rinse with methanol: Methanol ≥99.9%, B&J, Purge and Trap Grade 99.9% (min. by GC). For analysis of trace volatile organic compounds. Purgeable Organics 1 ng/L. Burdick & Jackson, part number: 232-1L

9.6.4 Air dry overnight or for several hours in a clean fume hood or similar.

10.0 Reagents and standards

10.1 Any substitution of reagent and/or standards from the suggested materials in this method are permitted but documentation of equivalency must be provided. Catalog numbers are included for illustration only.

10.2 Reagent water must be demineralized water that has been boiled in the laboratory, while simultaneously purged with ultra-high pure helium. Boiling for an additional 5 minutes is required after water reaches the boiling point. It is recommended that ultra-pure Type I water (18.2 MΩ.cm at 25 oC, total organic carbon (TOC) < 5 ppb), to be used for this method. When an alternative grade of water is used, the method performance must be verified prior to use in field samples.

10.3 Methanol: Methanol ≥99.9%, B&J, Purge and Trap Grade 99.9% min. by GC. For analysis of trace volatile organic compounds. Purgeable Organics 1ng/L. Burdick & Jackson, part number: 232-1L (VWR Catalog number: BJ232-235).

10.4 Ascorbic acid, 99%, VWR, catalog number: BDH9242-100G, or equivalent.

10.5 Concentrated Hydrochloric acid (HCl), 12.0 N, RICCA, VWR, product number: RCR3780000-1A.

10.6 Hydrochloric acid 1:1 v/v solution: Carefully add a measured volume of concentrated HCl to an equal volume of reagent water. Cool in ice bath as required.

10.7 Stock standards

10.7.1 1,2,3-TCP stock standard: 1,2,3-Trichloropropane standard, 100 mg/L, Agilent, part number: HC-440-1

10.7.2 ISTD: Cambridge Isotope Laboratories: 1,2,3-Trichloropropane (D5, 98%), purity 95%, 1 mg/mL in methanol, item # DLM-2080-1.2.

10.8 Calibration Standards Solutions

10.8.1 The primary dilution standard (PDS) is 100 µg/L: Prepare the PDS in methanol using 10 mL volumetric flask and the stock standard solution (10.7.1) according to the table below.

Stock conc. (mg/L)	Stock vol. (µL)	Final vol. (mL)	PDS Conc. (µg/L)
100	10	10	100

10.8.2 ISTD solutions:
The ISTD should be diluted to a final concentration of 200 µg/L via two serial dilutions.

10.8.2.1 First dilution (ISTD-PDS1) is from 1000 mg/L to 200 mg/L.

ISTD Stock conc. (mg/L)	Vol. of ISTD stock (µL)	Final vol. (mL)	ISTD-PDS1 conc.
1000	200	1	200

10.8.2.2 The second dilution (ISTD-PDS2) is 200 mg/L to 200 µg/L.

ISTD-PDS1 conc. (mg/L)	Vol. of ISTD PDS1 conc. (µL)	Final vol. (mL)	ISTD -PDS2 conc. (µg/L)
200	5	5	200

NOTE: Fill the second reservoir of the autosampler with ISTD PDS2.

10.9 Calibration standard solutions preparation:

10.9.1 Calibration standards are prepared in volumetric (Grade A) glassware at room temperature, 100 mL volumetric flasks. Fill seven flasks to nearly full (~ 99 mL) with laboratory reagent water. Add appropriate volumes of the PDS to the flasks, as shown in the Table below. Adjust the volume of the flasks to 100 mL with the reagent water and mix gently by inverting the flasks several times.

10.9.2 All calibration standards are prepared from the PDS (10.8.1)

Cal. Std.	PDS (µg/L)	Vol. of PDS (µL)	Final vol. (mL)	Cal. Std. (ng/L)
1	100	2	100	2
2	100	5	100	5
3	100	10	100	10
4	100	20	100	20
5	100	40	100	40
6	100	60	100	60
7	100	100	100	100

11.0 Sample collection, preservation, shipment, and storage

11.1 Sample collection

11.1.1 Samples are collected in duplicate in 40 mL amber VOA vials with PTFE- lined silicon septum cap, pre-cleaned to EPA level 2 specifications. Add 25 mg of dechlorinating agent (ascorbic acid) to each vial (Section 11.2).

11.1.2 Samples collected from a water tap (remove the aerator if any), must be flushed for approximately 15 minutes or until the water temperature stabilizes at an adjusted flow rate with laminar flow, no air bubbles are visually detected in the flowing stream. This requires a low flow rate (about 500 mL/min). A FD sample should be collected with appropriate dechlorinating agent immediately after collection of the first sample.

11.1.3 Partially filled 1-quart wide-mouth bottles or 1-L beakers can be used to collect water from open water sources. Rinse the bottle or beaker with the source water prior to collection of the sample.

11.1.4 Sample vials should be filled just to overflowing with an obvious positive meniscus, appropriate measures should be taken to not flush out the dechlorinating agent from the vial. After capping the vials they must be checked for the absence of air bubble(s), no air bubble greater than the size of a pea (≤ ¼-inch) should be trapped in the vial. Presence of air bubbles in the vial can be checked by turning the vial upside down after capping.

11.1.5 All sampling events are accompanied with a trip blank (TB) that is prepared in the laboratory and sent with the vials for sample collection. The TB must not be opened in the field during sampling.

11.2 Sample preservation

11.2.1 25 mg of ascorbic acid per 40 mL of sample is added to the sample vial for dechlorination prior to sample collection. Diethyl-p-phenylenediamine (DPD) test kits can be used in the field to determine residual chlorine. In the presence of >5 mg/L chlorine an additional 25 mg of ascorbic acid should be added for the dechlorination step.

11.2.2 Acidification of sample(s) after collection is recommended, but not required. This step eliminates any possibility of biotransformation of the analyte, during sample transfer and storage. If the laboratory choses to use sample acidification, a 6 M hydrochloric acid solution is included when sample collection materials are shipped to the sample collector. Immediately after sample collection, 3 drops of 6 M hydrochloric acid are added to the sample and mixed after capping. Note: the ascorbic acid and the HCl should not be mixed in the bottle prior to sampling.

11.2.3 Samples with high dissolved carbon dioxide may foam or bubble with addition of hydrochloric acid. In this situation, the sample must be collected without the addition of hydrochloric acid.

11.2.4 After sample collection, the sample containers must be chilled and kept at 4 – 6 °C until analysis. If the samples are not delivered to the laboratory for

analysis on the same day of collection, the samples should be maintained at 4 – 6 °C. The cooler used for shipping should contain enough ice to maintain a temperature around 4 °C and enough ice should remain in the cooler until delivery to the laboratory. Do not expose the samples to continuous direct sunlight and do not freeze them.

11.3 Sample storage

11.3.1 All samples, including TBs, are stored at 4 - 6°C at a location free of organic solvent vapors and without direct/intense lighting.

11.3.2 Maximum holding time after collection and preservation is 14 days.

11.3.3 Maximum holding time for an unpreserved (absence of ascorbic acid) collected sample is 24 hours.

12.0 Quality control

QC requirements include Initial Demonstration of Capability and ongoing QC requirements. This section describes each QC parameter and the performance criteria that must be met as described in Section 19.0. These QC criteria are the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

12.1 Initial demonstration of capability (IDC)

12.1.1 An IDC study must be conducted for each analyst and on each instrument performing this method before analyzing field samples.

12.1.2 A representative fortified concentration within the range of 20 -50 ppt, is selected to fortify reagent water samples. 4-7 LRB sample replicates are prepared in the same manner and analyzed in the same day or consecutive days.

12.1.3 IDC study samples must be treated as regular field samples and IDC run sequences must include all required QCs.

12.2 Method Detection Limit (MDL)

12.2.1 MDL determinations shall be performed at least annually and are valid until any deviations to the method, change of the analyst or the system are made.

12.2.2 The MDL calculation procedure can be reviewed from U.S. EPA publication titled: “Procedure for the Determination of the Method Detection Limit, Revision 2, 2016” (Reference 23.1).

12.3 A potable water Performance Evaluation (PE)/Performance Testing (PT) sample is recommended to be successfully analyzed at least annually. The PT sample must have a final concentration of 1,2,3- TCP in the range of 5-100 ng/L.

12.4 Laboratory reagent blank (LRB)/Method Blank: The LRB should be free from interferences that would prevent the determination of any analyte. The analyte concentration must be < 1/3 MDL. Analyze one LRB per batch of 20 or fewer samples or whenever reagents are changed. A LRB must be analyzed with each

sample batch in order to characterize contamination anywhere in the analytical process and/or system (e.g., vials, glassware, reagents, trap, column, detector).

12.5 Trip blank (TB): A trip blank must be analyzed with each set of field samples or for each source of testing and treated as a field sample. The TB should not have detectable interferences that would prevent the determination of the analyte (19.10). The purpose of the TB is to assess contamination introduced during collection, shipping, and storage.

12.6 Laboratory fortified blank (LFB): Prepare at 10 ng/L. An LFB must be analyzed at a minimum of one per batch of 20, or fewer samples.

12.7 Duplicate samples: A duplicate sample can be an LFB, a CCC, a FD or any sample run in duplicate in a batch. A duplicate sample is required to assess the methodology precision. A duplicate sample must be analyzed at a minimum of one per batch of 20 or fewer samples. If a field sample is above the MCL value, a FD is recommended for results verification.

12.8 Laboratory fortified sample matrix (LFSM): An LFSM must be analyzed if matrix effects are observed (Section 16.12.4). The spike level of the LFSM should be at the same level or higher as the LFB at 10 ng/L, and should not be less than the background level, if any, as determined in the TB of the specific sample analyzed.

12.9 Quality Control Sample (QCS): A quality control sample must be run with each batch of samples of 20 or fewer to check the accuracy of the procedure. For spiking the QCS the following formulations or equivalent can be used from certified commercial sources if available.

12.9.1 QCS standard: Accustandard (PN: APP-9-208), or ERA (PN: 682) or equivalent.

12.9.2 Prepare QCS at a concentration of 10 ng/L. The measured concentration must pass quality control criteria (Section 19).

12.9.3 The measured concentration of a QCS must be within the acceptable ranges of the method (Section 19.14).

13.0 Calibration and standardization

13.1 Instrument calibration or Instrument tune: Calibrate the MS, utilizing calibration compounds and procedures recommended by the manufacturer with any modifications necessary to meet tuning requirements. In this application, the MS is calibrated prior to every batch of samples using a commercial solution, FC-43 (part number: 05971-60571 from Agilent Technologies) also referred to as tune solution or instrument calibration solution. The tune compound reservoir is refilled approximately quarterly or even semiannually depending on the number of analyses performed. The instrument calibration procedure or tune is performed automatically applying a specific algorithm provided by the manufacturer. Agilent single quadrupole instrument is calibrated according to EPA 524.2 (Section 24.3).

13.2 Specific parameters for both the autosampler and P&T system (Section 24, Table 1 and 2 accordingly) are established for sample analysis. For the GC-MS operation refer to the instrument parameters outlined in Tables 3-7 (Section 24).

13.3 Initial multipoint calibration

13.3.1 As described in Section 14, run each calibration standard (Section 10.9.2) and use the GCMS data system software (Sections 9.2.4.1 and 9.2.4.2) to multipoint calibrate the system.

13.3.2 A response factor (RF) calculation (see equation below) for the analyte and the isotope pair for each CAL standard using the internal standard must be applied. This calculation is supported in acceptable GC-MS data systems software. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

$$RF = \frac{(A_X)\ (Q_{IS})}{(A_{IS})\ (Q_X)}$$

where: A_x = integrated peak area of the quantitation ion (m/z 75) of 1,2,3-TCP
A_{IS} = integrated peak area of the quantitation ion (m/z 79) of the 1,2,3-TCP-d5
Q_x = concentration of 1,2,3-TCP in ng/L
Q_{IS} = concentration of 1,2,3-TCP-d5 in ng/L.

13.3.3 The mean response factor (RF_{mean}) and standard deviation (SD) for all the calibration standards must be calculated (Section 16.1) and follow the quality criteria (Section 19.2).

13.3.4 As an alternative to calculating the RF_{mean}, a linear regression curve may be generated from the initial calibration data by plotting the ratio of A_x/ A_{IS} versus Q_x.
NOTE: The Chromeleon™ and MassHunter™ software automatically calculates the RF using the relationship between the area count and concentration of the target component (1,2,3- TCP) and area counts and concentration of ISTD (1,2,3-TCP-d5). In the multipoint calibration, the RF of target component for each calibration standard is averaged to provide the RF_{mean} which is used to calculate the concentration of target component in unknown samples as discussed in Section 16.2.

13.4 Continuing calibration check (CCC):

13.4.1 A CCC is prepared using a midpoint calibration standard or lower (e.g. 10 - 40 ppt), in the same manner as the LFB.

13.4.2 A CCC must be analyzed each day before beginning the sample batch analysis, and after every twentieth field sample. A CCC must always be analyzed at the end of the analysis sequence. Each batch of samples must be bracketed by CCC samples or LFB samples. For the acceptance criteria of the CCC sample see Section 19.8.

14.0 Procedure

14.1 Instrument setup: Set up the autosampler, purge and trap device and the GC-MS using the operating parameters outlined in Section 24, Tables 1 through 7. Allowed modifications are given in Section 15. Refer to Appendix III for a typical sequence of analysis. This method is designed for a 25 mL sparger volume and was tested

at the lower levels of detection with a 5 mL sparger volume (Table 1). Attention is required to the autosampler parameters which must be adjusted and applied appropriately for the use of 5 mL sparger.

14.2 System performance check: Before analyzing any calibration standards, run 3-4 LRBs to observe consistency and stability of the ISTD area count. If the area counts do not fall within the acceptable criteria (Section 19.5), follow steps in Sections 20.4 and 20.5.

14.3 Calibration standards (CAL): Transfer the calibration standards (Section 10.9) into pre-cleaned, pre- acidified (if acidification is used for sample collation) 40 mL VOA vials for analysis. Fill the vial to create a positive meniscus and gently close with the cap ensuring that there are no air bubbles trapped in the vial. Properly dispose any vial containing air bubbles. Store at 4oC until use. It is recommended to be used within 2 days of preparation.

14.4 Internal standard (ISTD): Fill reservoir 2 of the autosampler vial with ISTD-PDS 2 (Section 10.8.2.2). The ISTD-PDS 2 is injected by the autosampler automatically to all samples for analysis (at 40 ppt final concentration). For the appropriate method parameters for the autosampler refer to Table 1 in Section 24.

NOTE: If the autosampler does not have the capability to inject the ISTD to samples (CAL, QCs, field samples, etc.), the ISTD solution needs to be added manually to all samples. For a 25 mL or 5 mL sparger analysis, the volume of 20 µL or 8 µL respectively of ISTD-PDS 2 should be added to the calibration standards solutions (Section 10.9) and to the samples accordingly prior to analysis.

14.5 For the analysis of a batch of 20 samples, a typical sequence is provided as an example in Appendix III.

15.0 Procedure modifications

15.1 The laboratory is permitted to select autosampler and purge- and-trap concentrator conditions appropriate for the available instrumentation. The recommended parameters for 5 mL and 25 mL sparger are shown in Tables 1 and 2.

15.2 The gas chromatographic conditions can vary, but some key parameters are restricted. E.g. the type of the column should be DB-624 or have similar chemistry. A column with theoretical plates ≥4,630 plates/m (equivalent to a 20 m column I.D. <0.25 mm) is recommended to be used, and if possible, for fast GC applications ≤ 0.18 mm (20 m, 6,660 plates/m) should be used (see reference 23.6). When a short capillary column is used <30 m, as in this reference method, the laboratory must use the temperature program suggested (Table 4) due to possible observed interferences if otherwise.

Interferences must always be checked in trip blanks prior to field samples analysis. A signal is considered an interference when received in the same RT as the analyte and the quantitative ion is detected with SN >3 even if the ion ratio rule cannot be verified. A laboratory can use a longer temperature program as shown below to separate interferences chromatographically:

Rate (°C/min)	Value (°C)	Hold Time (min)	Run time (min)

	35	5	5
4	100	0.33	21.58
30	170	0	23.92

15.3 The mass spectrometric conditions are permitted to be altered (scan time, dwell time etc.) to accommodate appropriate instrumentation, except the ions for detection and quantitation. Specifically, all ions including 75, 110, and 112 are required to be monitored for 1,2,3-TCP and ions 79, 114, and 116 for deuterated 1,2,3-TCP. When there is an interfering compound at the masses of 75 both 110 and 112 ions must be used for quantitation and confirmation.

15.4 Modifications that result in poor method performance may not be used.

16.0 Data analysis and calculations

16.1 Initial Calibration: To assess the quality of the initial calibration, calculate or retrieve the RFmean value (from the system). Calculate the standard deviation (SD) and the relative standard deviation (RSD) for each standard: RSD = 100 (SD/RFmean). The QC criteria are given in Section 19.2.2.

16.2 The concentration of the unknown sample is calculated (following the equation below) using the multi-point calibration established in 10.9. The calibration verification sample data (CCC or LFB) must not be used for the calibration curve.

$$C_{TCP} = \frac{A_{TCP}\ Q_{TCP-D_5}}{A_{TCP-D_5}\ (RF_{mean})}$$

where C_{TCP} = concentration of 1,2,3-TCP in ng/L in the water sample
A_{TCP} = integrated peak area of the quantitation ion 75 of 1,2,3-TCP
$A_{TCP\text{-}d5}$ = integrated peak area of the quantitation ion 79 for the ISTD
$Q_{TCP\text{-}d5}$ = concentration of the ISTD in ng/L
RF_{mean} = mean response factor of the analyte from the initial calibration.

16.3 Alternatively use the GC-MS system software to calculate the concentrations of 1,2,3-TCP from the linear regression curve established in Section 10.9. In this method, the software calculates each component by RF_{mean} and linear regression. The setup parameters for calibration are in the processing method, component properties.

16.4 1,2,3-TCP is identified by matching the retention time (in this method 7.906 min for the unlabeled and 7.852 min for its labeled analogue however if the column is trimmed the retention times will change) and fragment ions and ion peak area ratios from the sample with those of the reference standards. Identification requires expert judgment, especially when sample components are not completely resolved, or if 1,2,3-TCP is present at very low concentration (near the method detection limit). Background ions or interfering ions from coeluting compounds may make identification (and quantitation) difficult to achieve. A typical chromatogram of 1,2,3-TCP and its ISTD based on their quantitation ions is shown in Appendix IV.

16.5 To monitor the retention time (RT), the available software is used accordingly. Specifically, the processing method is programmed to detect 1,2,3-TCP response peak within ±0.082 min (4.92 sec) of the assigned RT. For 1,2,3-TCP-d5, it is programmed to detect the response peak within ±0.066 min (3.96 sec) of the assigned RT. Different criteria can be implemented in coordination with the software used, but the RT windows are recommended to be set as narrow as possible. These criteria can only be adjusted if a longer column and/or a longer temperature program is applied.

16.6 1,2,3-TCP and 1,2,3-TCP-d5 are identified for each unknown sample using ion ratio rule. The mean peak area ratio of the m/z 75 ion to the m/z 110 ion of 1,2,3-TCP from the initial calibration or the daily CCC must be calculated for every analysis. The ion ratio of the sample should compare within ± 30% of the reference mean value. A reference spectra library comparison (NIST/EPA/NIH Mass Spectrometry library) can be used as identification tool if available, but the ion ratio rule must always be followed for confirmation. In either case, all monitored ions need to be present for identification. For 1,2,3-TCP, in multiple ion monitoring (MIM) mode, m/z 75, 110 and 112 are monitored. Additionally, for ISTD 1,2,3-TCP-d5, m/z 79, 114 and 116 are monitored.

16.7 When the level of identification is >MCL CA value, the mean peak area ratio of the m/z 75 ion to the m/z 110 ion, in addition to the mean peak area ratio of the m/z 110 ion to the m/z 112 ion of 1,2,3-TCP is required for verification.

16.8 For low levels of identification, i.e. <10 ppt the qualification ion must read at or above S/N=3 to have a confirmation, independent of the ion ratio identification.

16.9 CCC: Calculate the concentrations of each CCC sample similar to an unknown sample.

16.10 Duplicate sample: Calculate the relative percent deviation (RPD) of the samples as follows:

$$\mathrm{RPD} = \frac{|X_1 - X_2|\,100}{\bar{X}}$$

where X_1 and X_2 are the measurements of the two sample concentrations and $\bar{X}$ is the mean value of the two measurements.

16.11 QCS: Calculate the percent recovery of the QC sample.

16.12 When compiling the final report package, consider the following:

16.12.1 The lowest calibration standard must always be below or equal to the RL. For example, in this method the RL is 2 ppt as dictated by the lowest calibration standard of the calibration curve.

16.12.2 Reporting criteria should follow the quality assurance project plan of the laboratory. Typically, samples with detected levels below RL are reported as <RL.

16.12.3 If the laboratory has established a calibration standard at < RL, in order to report the result of an unknown sample using a calibration curve which

includes that calibration standard, two factors of verification of identity must be applied for that calibration standard: a) the QC criteria (Section 19.2) must be met and b) a S/N ration ≥ 3 for the confirmation ion of 1,2,3-TCP (m/z 110) must be identified. At low levels of <10 ppt the NIST library identification is not always accurate.

16.12.4 When an LFSM is required and the QC criteria (Section 19.13) are not met, the result for that sample is reported and flagged in the final report as failed to pass QC criteria due to suspected matrix effects.

17.0 Method performance

17.1 MDL: For this application, seven or more, samples spiked at 2 – 6 x the previous MDL value are prepared and analyzed over 3 non-consecutive days. The MDL is calculated according to Section 12.2.2. Monitoring MDL values over the years using charts provide insight to both instrument and method performance.

17.2 QC charts should be developed for the LFB samples after a sufficient number of data points have been collected for each, usually a minimum of results from 20 to 30 analyses. When sufficient internal performance data become available, develop control limits from the mean percent recovery (R) and standard deviation (SD) of the percent recovery. These data are used to establish upper and lower control limits as follows:

UPPER CONTROL LIMIT = R + 3SD

LOWER CONTROL LIMIT = R - 3SD

17.3 Additionally, the overall method performance can be verified by monitoring the results of blind PT studies.

17.4 Method performance has been validated in about 100 drinking water samples. 1,2,3-TCP was detected in ~30% of the analyzed samples in duplicate analyses with levels ranging from 2.93 to 22.8 ppt (Appendix V).

18.0 Pollution prevention

18.1 Perform all preparation of standards and samples under the fume hood. Discard remaining PDS, method samples (CAL, LFB, CCC, and QC), and field samples 48 hours after processing, in a closed glass container.

18.2 The only chemical used in this method (except the 1,2,3-TCP) that pose a threat to the environment is the hydrochloric acid used to preserve field samples. This chemical is used in small volumes and does not require additional consideration than those mentioned in Section 18.1.

18.3 Laboratory waste management practices must be conducted consistent with all applicable rules and regulations and laboratory should strive to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. In addition, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

19.0 Data assessment and acceptance criteria for QC measures

19.1 For quality control purposes, review the processed results and ensure that the QC criteria below are met before reporting results.

19.2 Acceptable calibration criteria.

19.2.1 The acceptance criteria for the calibration curve is R2 ≥ 0.995.

19.2.2 Acceptable criteria for the RSD of each analyte is +/- 20%.

19.2.3 Additionally, the calibration should be examined for fit by comparing the observed concentration at each calibration point with the expected concentration. As a guideline, the observed concentration for each calibration point should be within ± 20% of the true value, if not see Section 20.1.

19.2.4 A calibration point with a poor fit should not be discarded unless there is a justification, e.g., error in preparation, degradation of the analyte, solvent evaporation, or autosampler/purge and trap concentrator error.

19.3 The lowest calibration standard must always be ≤ RL and should be verified by the QC criteria above.

NOTE: Eliminating the lowest calibration point will affect the RL of the method, and the method may not meet the necessary regulatory requirements.

19.4 The chosen RL value must be within ± 20% of the true value, since the RL is within the calibration range, it should meet the criteria applied for any calibration standard. Further, the RL must be ≤CA DLR value and ≥ the lowest calibration point.

19.5 For the ISTD acceptance criteria, an average of the ISTD area count from the calibration standards is calculated. The acceptable criterion for the ISTD recovery is 80-120% of this average value.

19.6 For each analyzed sample the ISTD peak area response must be within ± 20% of the average peak area response of the ISTD of the calibration curve on the day of the analysis.

19.7 IDC: The average percent recovery of each LFB must fall within ± 20% of the expected concentration value. The RSD should be less than 30%.

19.8 CCC: measured concentration for both 1,2,3-TCP and the labeled analogue must be within 80-120% of the true concentration.

19.9 LRB: The measured concentration of the LRB must be < 1/3 MDL.

19.10 Trip Blank: the measured concentration must be < 1/3 MDL.

19.11 LFB: the measured concentration must be within 80 to 120% of the fortified concentration.

19.12 Duplicate samples: When a duplicate sample is analyzed within the same sequence, the RPD should be within ± 10%. If a duplicate sample is analyzed on a different day of analysis, the acceptance criteria is ± 20% or lower.

19.13 LFSM: the measured concentration must be within 70 - 130% of the fortified concentration.

19.14 QCS: The measured concentration must be within 80 - 120% of the fortified concentration. When a QC sample is purchased from a certified reference materials source, the acceptable value must fall within 80 - 120% recovery of the Certified Value. See below as an example provided for an ERA QC sample:

Parameter	Certified Value (ng/L)	Uncertainty (%)	QC[1] Performance Acceptance Limits (ng/L)	PT Performance Acceptance Limits (ng/L)	DWRL_123TCP QCS Acceptance Limits (ng/L) (80-120%)
1,2,3-TCP	19.3	0.97	13.4-24.7	11.6-27.0	15.4-23.2

[1]Product: WatR™ Supply Low-Level 1,2,3-TCP, Catalog number 682, Lot number: S270-682

19.15 When the measured concentration of an unknown sample is ≥ MCL, the laboratory management must be notified immediately.

20.0 Corrective actions for out-of-control data

20.1 For the calibration curve, if the RSD of the analyte or RFmean does not meet the acceptance criteria (value outside of 20%), analyze new calibration standards to obtain an acceptable value over the entire concentration range. A new FC-43 instrument tune might be required. If the QC criteria still are not met, evaluate the system performance by proceeding to check the system maintenance actions such as: clean or replace splitless injection liner, flush the column with solvent or bake the column overnight, cut a short portion from the front end of the column near to injector, or replace the GC column, prepare fresh CAL standards and recalibrate the system, clean the MS source, replace the electron multiplier or any other faulty components. The remedial actions should take place in the above order.

20.2 When the RL quality criteria are not met, a new RL value must be determined until it fits the required acceptable criteria.

20.3 When the QC criteria of any of the parameters presented in Section 19 are not met, ISTD area count reproducibility (%RSD) needs to be verified. ISTD area count inter-day precision can fluctuate ±20% compared to the averaged ISTD counts from calibration standards. When that is observed, the instrument must be recalibrated, preparation of a fresh ISTD solution may be necessary, and the analysis must be repeated.

20.4 When the ISTD reproducibility fails to meet the quality criteria in Section 19.6, the system must be recalibrated, and the analysis repeated.

20.5 When ISTD reproducibility continues failing to meet the quality criteria (Section 19.5 & 19.6), and after remedial actions suggested in Section 20.3 have taken place, check if MS ion source is in clean condition. To clean the MS ion source, per manufacturer's MS ion source recommendation, the MS is turned off and vented prior to removing the ion source from the MS. The ion source is disassembled, gently cleaned with aluminum oxide, sonicated in different solvents

and water, and dried. Afterwards, the ion source parts are assembled and re-installed. The MS is pumped down overnight to up to 24 hours.

20.6 When more than one parameter from Section 19 does not meet the criteria and especially when the initial calibration curve fails to meet the acceptance criteria in Section 19.2, the analyst must inspect the system for proper operating conditions, including the autosampler (e.g. needle position, etc.), the purge and trap system (e.g., trap replacement, bake out, etc.), and/or the GC-MS system (e.g. liner replacement, column bake out, new tune, etc.). After the appropriate maintenance is performed, the system must be recalibrated with freshly prepared calibration standards.

20.7 If the highest or lowest calibration point is removed due to poor fit but results in quantification of a sample falls outside the calibration range, recalibrate the system using freshly prepared standards so that the sample falls within the calibration range.

20.8 If 1,2,3-TCP is detected in LRB at a value greater than one-third of the MDL value (monitoring just the ion m/z 75 and even if the m/z is not detected or the ion ratio rule is confirmed), prepare a new ISTD solution from a different lot number or manufacturer. It is important to ensure that contamination from the ISTD with the native compound remains at acceptable levels. Thereafter, LRB is checked using the newly prepared ISTD solution.

20.9 When the Trip Blank has measurable concentrations of 1,2,3-TCP at levels > 1/3 MDL, but all the QC parameters of the analysis are meeting the QC criteria, a field sampling interference/contamination is suspected. Flag the results and arrange a resampling event when possible. If other QC parameters do not meet QC criteria and especially the LRB, see Section 20.3.

20.10 If a level of 1,2,3-TCP >MDL is detected in the LRB preceding a sample's run, then a duplicate of that sample should be analyzed. The analyst must not start a sample analysis batch until the LRB passes QC criteria.

20.11 Refer to Section 9.4 for the type of vials that are required for analysis. It is recommended to keep a record of all vials lot number(s) and the dates of analysis of the LRBs. If vials do not meet the criteria described in Section 9.4, an LRB prepared using a vial from the lot must be analyzed and results documented per lot number.

20.12 Conflicting results obtained under ideal conditions can be likely traced to improper standard preparation and/or matrix effects. Preparing fresh calibration standards can easily verify the validity of the initial calibration curve.

21.0 Contingencies for handling out-of-control or unacceptable data

21.1 If the lowest calibration point or highest point fails to meet the calibration acceptance criteria, the lowest calibration point or highest point can be removed. The lowest or the highest calibration points cannot be removed if the QC criteria are met and a clear reason for failure is not justified. When removing the lowest calibration point attention should be given that there is a calibration point below the RL, and if not, the lowest calibration point is set as the new RL.

21.2 If a sample analyte concentration falls out of the calibration range after removing the highest point, the sample duplicate needs to be analyzed after recalibrating the system to include the sample concentration within the calibration range.

21.3 When QC does not meet the criteria in Section 17.2, continue to resolve the issue with these actions:

21.3.1 Revise and recheck QC sample preparation steps.

21.3.2 Repeat sample preparation and prepare a new QC sample

21.3.3 If none of the above resolve the issue, re-tune mass spectrometer and build new calibration curve, respectively, if needed.

21.4 If the reason for unacceptable data is determined to be system related (e.g., detector malfunction) and cannot be resolved by the analyst, conduct troubleshooting steps and/or contact instrument vendor for technical support and setup a field service visit if necessary.

21.5 If unacceptable data is determined to be matrix related (e.g., all other QC criteria are met but not LFSM recovery) and cannot be resolved by corrective actions given in Section 20, report the data with a flag for further review.

22.0 Waste management

22.1 Dispose waste containers within three months or earlier of waste collection start date. Containers must be always closed and kept inside the hood.

23.0 References

23.1 US. EPA, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2, December 2016

23.2 EPA. 1992. “Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry,” Revision 4.0.

23.3 DWRL method SRL524M, Determination of 1,2,3-Trichloropropane in drinking water by purge and trap gas chromatography/mass spectrometry”, H.S Okamoto, W.R. Steeber, J. Remoy, P. Hill, S.K. Perera, February 2002.

23.4 Clin Biochem Rev. 2008 Aug; 29(Suppl 1): S49–S52.

23.5 EPA Technical Fact Sheet- 1,2,3-Trichloropropane (TCP), EPA 505-F-14-007, January 2014.

23.6 Agilent Technologies, Simon Jones, “Secrets of GC column dimensions”, May 20, 2008.

24.0 Tables, diagrams, flowcharts and validation data

24.1 Autosampler parameters:

Table 1: Autosampler parameters

	EST	EST	AtomxXYZ
Sample Volume	25 mL	5 mL	25 mL
Sample Type	Water	Water	Water
Sample Fill Mode	LOOP	LOOP	Syringe
Sample Loop Fill Time (sec)	37	20	
Loop Equilibration Time (sec)	5	5	
Sample Transfer Time (sec)	45	15	
Needle Rinse Time (sec)	20	20	
Needle Sweep Time (sec)	10	10	
Sample Loop Rinse Time (sec)	30	20	
Sample Loop Sweep Time (sec)	45	15	
Concentrator Desorb Time (sec)	60	60	
Number of Sparge Rinse Cycles	2	2	3
Rinse Transfer Time (Sec)	40	20	
Rinse Drain Time (sec)	40	25	
Number of Foam Rinse Cycles	3	3	
Concentrator #1 Cycle Time (min)	0	0	
Water Heater Temperature	85	85	

Table 2: EST Analytical Encon Evolution Purge and Trap Concentrator Parameters (25 mL or 5 mL sparger)

	EST	AtomxXYZ
Trap Ready Temperature (˚C)	35	
MoRT Ready Temperature (˚C)	39	
Purge Flow Rate (mL/min)	40	40
Purge Time (min)	11	11
Dry Purge Temperature (˚C)	Off	20
Dry Purge Flow Rate (mL/min)	40	100
Dry Purge Time (min)	1	2
Desorption Pressure Control (psi)	On at 5	
Desorption Flow Control (psi)	Off	
Desorption Preheat Temperature (˚C)	245	245
Desorb Temperature (˚C)	250	250
Desorb Time (min)	2	2
Trap Bake Temperature (˚C)	260	260
MoRT Bake Temperature (˚C)	210	200
Bake Flow Rate (mL /min)	85	400
Bake Time (min)	7	3
Bake Cycles	1	

	EST	AtomxXYZ
Overfill	Off	
Foam Sensor	Off	Off
GC Cycle Time (min)	0	
Start Delay (min)	0	
Economy Mode	Off	
Standby Flow (ml/min)	40	
Automatic Drain Sparge Vessel	On	
Bake Gas Bypass	Off	
Transfer Line Temperature (˚C)	150	150
Valve Oven Temperature (˚C)	150	150
Auto Sample Prep Time (min)	0	
Sample Heater Type	On,Vessel	
Pre-Purge Time (min)	0	
Preheat Temperature (˚C)	0	
Preheat Time (min)	0	
Purge Temperature (˚C)	Off	
Bake Temperature (˚C)	40	

24.2 GC parameters:

Table 3: GC inlet

	Thermo GC 1310	Agilent GC 8890
Operating mode	Split	Split
Split flow control	On	On
Split flow	28.0 mL/min	14 mL/min
Split ratio	1:35	1:20
Purge flow control	On	On
Purge flow	0.5 mL/min	5 mL/min
Vacuum compensation	On	blank
Enable gas saver mode	On	Off
Gas Saver Flow	25.0 mL/min	blank
Gas saver time	5.00 min	blank

Table 4: GC oven settings

Retention time (min)	Rate (˚C/min)	Target value (˚C)	Hold time (min)
3	0	60	3
16.313	16	225	0.33
17	Stop run		

24.3 Mass spectrometer parameters

Table 5: Mass spectrometer mode and relevant parameters for Thermo GC (1310) MS TSQ 8000Duo

Mode	SIM
Range m/z	N/A
Selected m/z	75, 79, 110, 112, 114,116
Dwell time (ms)	30, 30, 30, 30, 30,30
Scan time (sec)	N/A
Total scan time	0.1617
Detector gain	7.00E+05
Chromatogram start time (mins)	5.00

Table 6: Mass spectrometer mode and relevant parameters for Agilent GC (8890) MSD (5977B) (Ion abundance criteria is evaluated using 4-Bromofluorobnznes (BFB)).

Mode	SIM
Range m/z	N/A
Selected m/z	75, 79, 110, 112, 114
Dwell time (ms)	100, 50, 100, 100, 50
Gain Factor	5
Chromatogram start time (mins)	6.00

Table 7: Additional mass spectrometer parameters

Ion optics temp	274˚C
Repeller	
Repeller voltage	0.0 V
Filament	
Electron lens voltage	5.0 V
Electron energy	70.0 V
Lenses	
Lens 1 voltage	0.0 V
Lens 2 voltage	0.0 V
Lens 3 voltage	0.0 V
Ion guide	
Ion guide voltage	0.0 V
Ion guide frequency	1676 kHz
Ion guide RF amplitude	0.0 V

Q1	
Q1 entrance lens voltage	0.0 V
Q1 voltage	50.0 V
Q1 frequency	1088 kHz
Q1 RF amplitude	0.150 V
Q1 exit lens voltage	0.0 V
Q2	
Q2 voltage	-150.0 V
Q2 frequency	1865 kHz
Q2 RF amplitude	0.020 V
Q3	
Q3 entrance lens voltage	0.0 V
Q3 voltage	0.0 V
Q3 frequency	1086 kHz
Q3 RF amplitude	0.058 V
Q3 exit lens voltage	0.0 V
Dynode/Multiplier	
Multiplier voltage	0 V
Dynode voltage	-10.0 kV

25.0 Appendices

I. MDL performance with Thermo Fisher GC (Trace 1310) MS TSQ 8000Duo (performed with 25 mL sparger at 2 ng/mL spiked concentration). MDL = 0.30 ppt

	Date	Experimental value 1,2,3-TCP (ng/L)
Test 1	1/23/2020	1.85
Test 2	1/23/2020	2.1
Test 3	1/23/2020	1.95
Test 4	1/23/2020	1.85
Test 5	1/24/2020	1.9
Test 6	1/24/2020	1.98
Test 7	1/27/2020	1.96
Test 8	1/27/2020	2.12
Test 9	1/27/2020	1.87
Average		1.95
STDev		0.1
RSD%		5.21
MDL (2.998XSTDev)		0.30

Abbreviations: STDev= Standard Deviation, RSD =Relative Standard Deviation

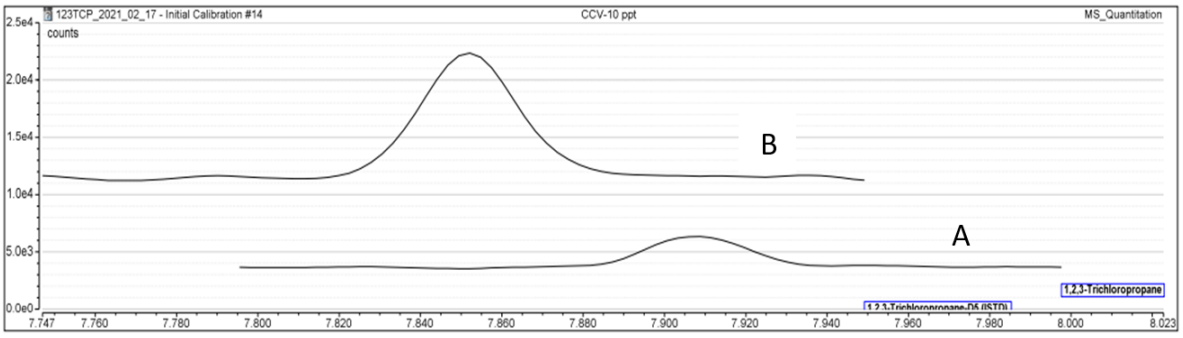
II. MDL performance with Teledyne Tekmar Atomx XYZ & Agilent GC (8890) MSD (5977B) (performed with 25 mL sparger at 2 ng/mL spiked concentration). MDL = 0.33 ppt

MDL-spike		**MDL-blank**	
Date	Experimental Value 1,2,3-TCP (ng/L)	Data	Experimental Value 1,2,3-TCP (ng/L)
20210315	2.08	20210316	0.19
20210315	2.24	20210316	0.12
20210315	2.3	20210316	0.23
20210317	2.04	20210317	0.16
20210317	2.09	20210317	0.2
20210317	2.27	20210319	0.25
20210319	2.2	20210319	0.2
Average (ppt)	2.17	Average (ppt)	0.19
Std Dev	0.1	Std Dev	0.04
Spiked amount (ug/mL)	2		
MDLs (ppt) (= t X Std Dev)	0.32	MDL_b (ppt) (= Average+ t X Std Dev)	0.33
MDL< Spiked values	Yes		
Spiked Values < 10X MDL	Yes		

III. Typical Autosampler Queue for Sample Analysis (batch of 8 samples)

No.	Sample Name	Sample Type
1	Reagent water blank	Water blank
2	LFB/CCC – 10 µg/L	Initial calibration verification check
3	Reagent water blank/Blank/Method blank	Water Blank
4	Sample 1-TB	Field sample
5	Sample 1	Field sample
6	Sample 2-TB	Field sample
7	Sample 2	Field sample
8	Sample 3-TB	Field sample
9	Sample 3	Field sample
10	Sample 4-TB	Field sample
11	Sample 4	Field sample
12	Sample 5-TB	Field sample
13	Sample 5	Field sample
14	Sample 5 duplicate	Field duplicate
15	Reagent water blank (LRB)	Water blank
16	QCS	Quality control sample
17	Sample 6-TB	Field sample
18	Sample 6	Field sample
19	Sample 7-TB	Field sample
20	Sample 7	Field sample
21	Sample 8-TB	Field sample
21	Sample 8	Field sample
23	LFB/CCC	Continuing calibration verification
24	Reagent water blank	Water blank

IV. Typical Chromatogram of 1,2,3-TCP (10 ppt) (A), RT= 7.906 and 1,2,3-TCP-d5 (40 ppt) (B), RT = 7.852



V. Data from real samples analysis and their duplicate values. All duplicates were run the same day as the original samples (performed with 25 mL sparger).

Sample (ppt)	Sample Dup. (ppt)	Avg	RPD (%)
2.93	2.99	2.96	2.05
10.9	11.3	11.1	3.38
17.2	16.5	16.8	4.46
21.4	21.6	21.5	1.05
10.7	9.91	10.3	7.36
4.96	4.74	4.85	4.63
7.94	6.97	7.46	12.96*
7.53	7.04	7.28	6.73
5.92	6.26	6.09	5.53
22.9	16.2	19.5	34.15
7.53	7.04	7.28	6.73
5.92	6.26	6.09	5.53
17.2	16.5	16.8	4.46
21.4	21.6	21.5	1.05
10.7	9.91	10.3	7.36
4.96	4.74	4.85	4.63
7.94	6.97	7.46	12.96*
7.53	7.04	7.28	6.73
5.92	6.26	6.09	5.53
22.9	16.2	19.5	34.15*
13.4	12.9	13.2	3.75
13.6	14.9	14.2	6.51
11.6	13.5	12.5	10.4

*Samples analyzed the same day of analysis with % RPD ≥ 10% are flagged in final reports.