



# A Review of Distribution System Chlorine and Chloramine Methods

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Newport News Waterworks

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# Motivation for Talk

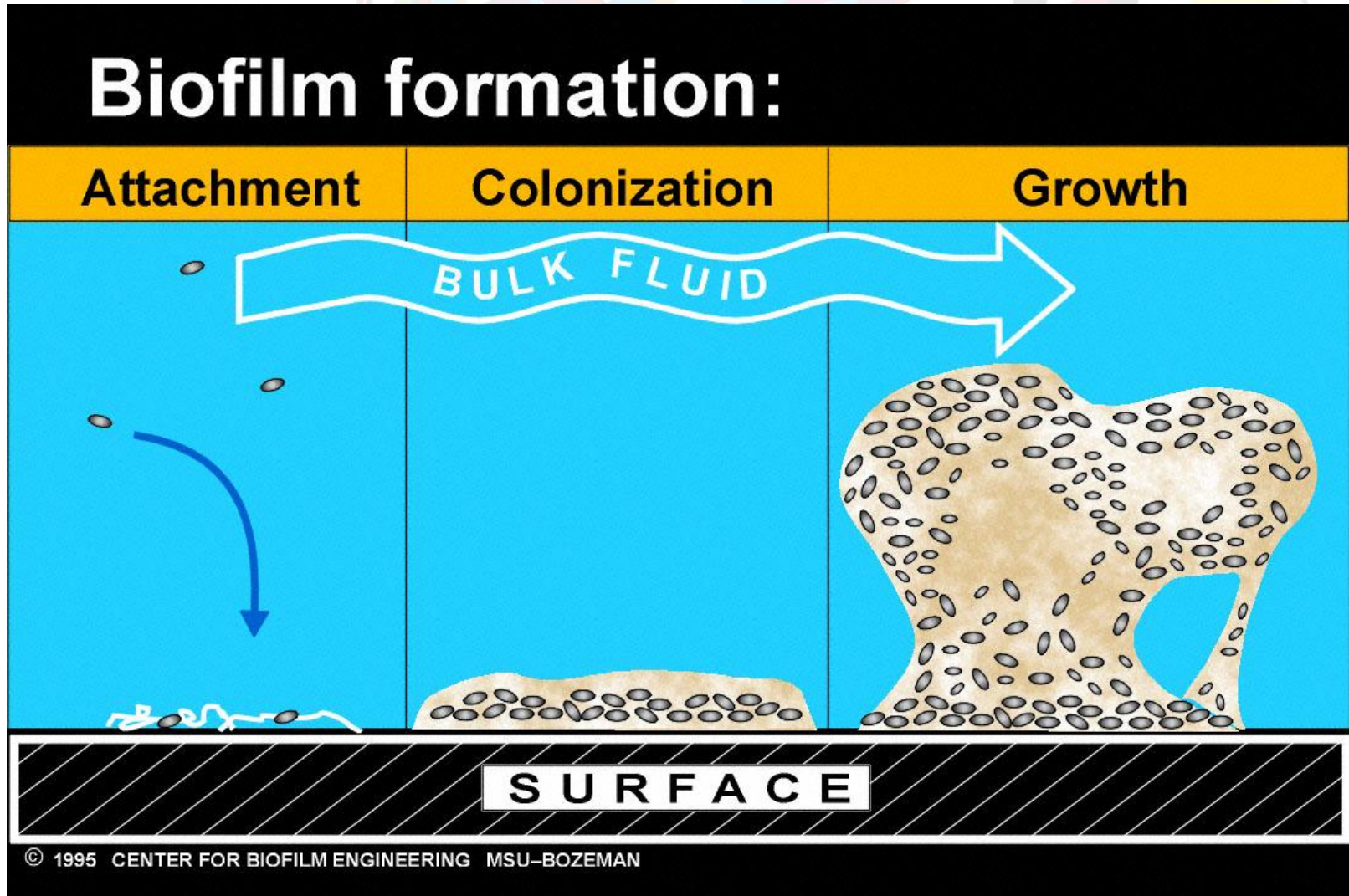


- There is a perceived public health vulnerability related to the growth of biofilm organisms.
  - Legionella
  - Naegleria Fowleri
- Tools to fight biofilms
  - Low amount of nutrients in finished water
  - Main break management
  - Pressure management
  - Residual disinfectant management

# Residual Disinfectant Management

- Primary disinfection at plants is governed by CT for a particular disinfectant
  - CT tables developed for ozone, free chlorine, monochloramine and chlorine dioxide
  - Inactivation of giardia, cryptosporidium (ozone) and viruses is achieved by the disinfectant in the bulk water in the disinfection contactor.
- Goals of secondary disinfection
  - Minimize mass of biofilm in system
  - Inactivate any living particles that are released from the biofilm into the bulk water in the pipes.

# Biofilm Formation



# Assumptions

- The higher the free chlorine or monochloramine residual, the lower the overall mass of the biofilm in the system will be.
- The higher the free chlorine or monochloramine residual, the more effective the inactivation of any living particles released from the biofilm will be.
- Measurement of free chlorine, total chlorine or monochloramine residuals is an indication of how well we are managing our biofilms.

# Approved Methods for Free and Total Chlorine

- SM 4500-Cl D Amperometric Method
- SM 4500-Cl G DPD Method
- DPD is the generally preferred method as it is operationally simpler than the amperometric titration.

# Expedited Analytical Rule

**B. What is the basis for this action?**

When EPA determines that an alternative analytical method is "equally effective" (i.e., as effective as a method that has already been promulgated in the regulations), SDWA allows EPA to approve the use of the alternative method through publication in the **Federal Register** (see Section 1401(1) of SDWA). EPA is using this streamlined approval authority to make 16 additional methods available for determining contaminant concentrations in drinking water samples collected under SDWA. EPA has determined that, for each contaminant or group of contaminants listed in Section III, the additional testing methods being approved in this action are as effective as one or more of the testing methods already approved in the regulations for those contaminants. Section 1401(1) of SDWA states that the newly approved methods "shall be treated as an alternative for public water systems to the quality control and testing procedures listed in the

regulation." Accordingly, this action makes these additional 16 analytical methods legally available as options for meeting EPA's monitoring requirements.

This action does not add regulatory language, but does, for informational purposes, update an appendix to the regulations at 40 CFR part 141 that lists all methods approved under Section 1401(1) of SDWA. Accordingly, while this action is not a rule, it is updating CFR text and therefore is being published in the "Final Rules" section of the **Federal Register**.

**III. Summary of Approvals**

EPA is approving 16 methods that are equally effective relative to methods previously promulgated in the regulations. By means of this rule, these 16 methods are added to appendix A to subpart C of 40 CFR part 141.

*A. Methods developed by Voluntary Consensus Standard Bodies (VCSB)*

ASTM International. EPA compared the most recent versions of seven ASTM

International methods to the earlier versions of those methods that are currently approved in 40 CFR part 141. Changes between the earlier approved version and the most recent version of each method are summarized in Smith (2015). The revisions primarily involve editorial changes (e.g., updated references, definitions, terminology, procedural clarifications, and reorganization of text). The revised methods are the same as the approved versions with respect to sample collection and handling protocols, sample preparation, analytical methodology, and method performance data; thus, EPA finds they are equally effective relative to the approved methods.

EPA is thus approving the use of the following ASTM methods for the contaminants and their respective regulations listed in the following table:

ASTM revised version	Approved method	Contaminant	Regulation
D 1253-14 (ASTM 2014a) .....	D 1253-03 (ASTM 2003a) .....	Free Chlorine; Total Chlorine .....	40 CFR 141.74(a)(2); 40 CFR 141.131(c)(1).
D 1253-14 (ASTM 2014a) .....	D 1253-03 (ASTM 2003a) .....	Combined Chlorine .....	40 CFR 141.131(c)(1).
D 1125-14 A (ASTM 2014b) .....	D 1125-95 A (ASTM 1995) .....	Conductivity .....	40 CFR 141.23(k)(1).
D 511-14 A (ASTM 2014c) .....	D 511-03 A (ASTM 2003b) .....	Calcium; Magnesium .....	40 CFR 141.23(k)(1).
D 511-14 B (ASTM 2014c) .....	D 511-03 B (ASTM 2003b) .....	Calcium; Magnesium .....	40 CFR 141.23(k)(1).
D 1688-12 A (ASTM 2012a) .....	D 1688-02 A (ASTM 2002a) .....	Copper .....	40 CFR 141.23(k)(1).
D 1688-12 C (ASTM 2012a) .....	D 1688-02 C (ASTM 2002a) .....	Copper .....	40 CFR 141.23(k)(1).
D 3697-12 (ASTM 2012b) .....	D 3697-02 (ASTM 2002b) .....	Antimony .....	40 CFR 141.23(k)(1).

The ASTM methods are available from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959 or <http://www.astm.org>.

**B. Methods Developed by Vendors**

1. Hach Method 10241—Spectrophotometric Measurement of Free Chlorine (Cl<sub>2</sub>) in Finished Drinking Water (Hach Company 2015a). In Hach Method 10241, free chlorine is converted to monochloramine by addition of an ammonia solution to a drinking water sample. In the presence of a cyanoferrate catalyst, monochloramine reacts with a substituted phenol to form an intermediate monoamine compound. The intermediate monoamine compound couples with excess substituted phenol to form a green indophenol compound. Spectrophotometric measurement of absorbance at 655 nm (610 nm for colorimeters) is directly proportional to the concentration of free chlorine in the sample.

The currently approved methods for free chlorine in drinking water are listed in the tables at 40 CFR 141.74(a)(2) and 40 CFR 141.131(c)(1). One of the most widely used approved methods is Standard Method 4500-Cl G-00 (APHA 2000a), which uses a N,N-diethyl-p-phenylenediamine (DPD) indicator for spectrophotometric determination of residual chlorine concentrations in drinking water. The DPD methodology can be subject to interferences associated with the presence of manganese, chloramines, and other oxidants. Hach Method 10241 is not subject to such interferences.

A multi-laboratory study compared the performance characteristics of Hach Method 10241 to the performance characteristics of the approved Standard Method 4500-Cl G-00. A variety of samples, including drinking water samples from both surface water and ground water sources, were fortified with known chlorine concentrations and analyzed by each method. The results are summarized in the validation study report (Hach Company 2015b).

EPA has determined that Hach Method 10241 is equally as effective as the approved Standard Method 4500-Cl G-00. The basis for this determination is discussed in Adams and Smith (2016). Therefore, EPA is approving Hach Method 10241 for determining free chlorine concentrations in drinking water. Hach Method 10241 can be obtained from Hach Company, 5600 Lindbergh Drive, Loveland, Colorado 80539. (<http://www.hach.com>.)

2. Hach Method 8026—Spectrophotometric Measurement of Copper in Finished Drinking Water (Hach Company 2015c). In Hach Method 8026, cuprous copper is measured colorimetrically by complexation with bicinchoninic acid. The intensity in color is proportional to the copper concentration, and spectrophotometer measurements are taken at 560 nm. Cupric copper present in samples is chemically reduced to cuprous copper. Metal and hardness interferences in samples are mitigated through the use of a chelating agent. The method is performed by the addition of

# Interferences with Approved Methods

- There are numerous interferences with the DPD method, however the two most important ones are;
  - Oxidized manganese
    - Manganese is present in most finished waters and EPA has set a SMCL of 0.05 mg/l for total Mn.
    - Hach has a cumbersome work-around to eliminate the manganese interference.
  - Organic Chloramines
    - Organic chloramines show up in the total chlorine reading, but they are an ineffective disinfectant.

# Implications

- Total chlorine will always be higher than monochloramine reading due to presence of positive interferences.
- Surface Water Treatment Rule (SWTR) requires a “detectable” residual using the free and/or total chlorine test.
- At low levels of free and total chlorine, is there really any disinfectant there?
- Test for monochloramine directly.

# Hach SL1000 Portable Parallel Analyzer™ (PPA)

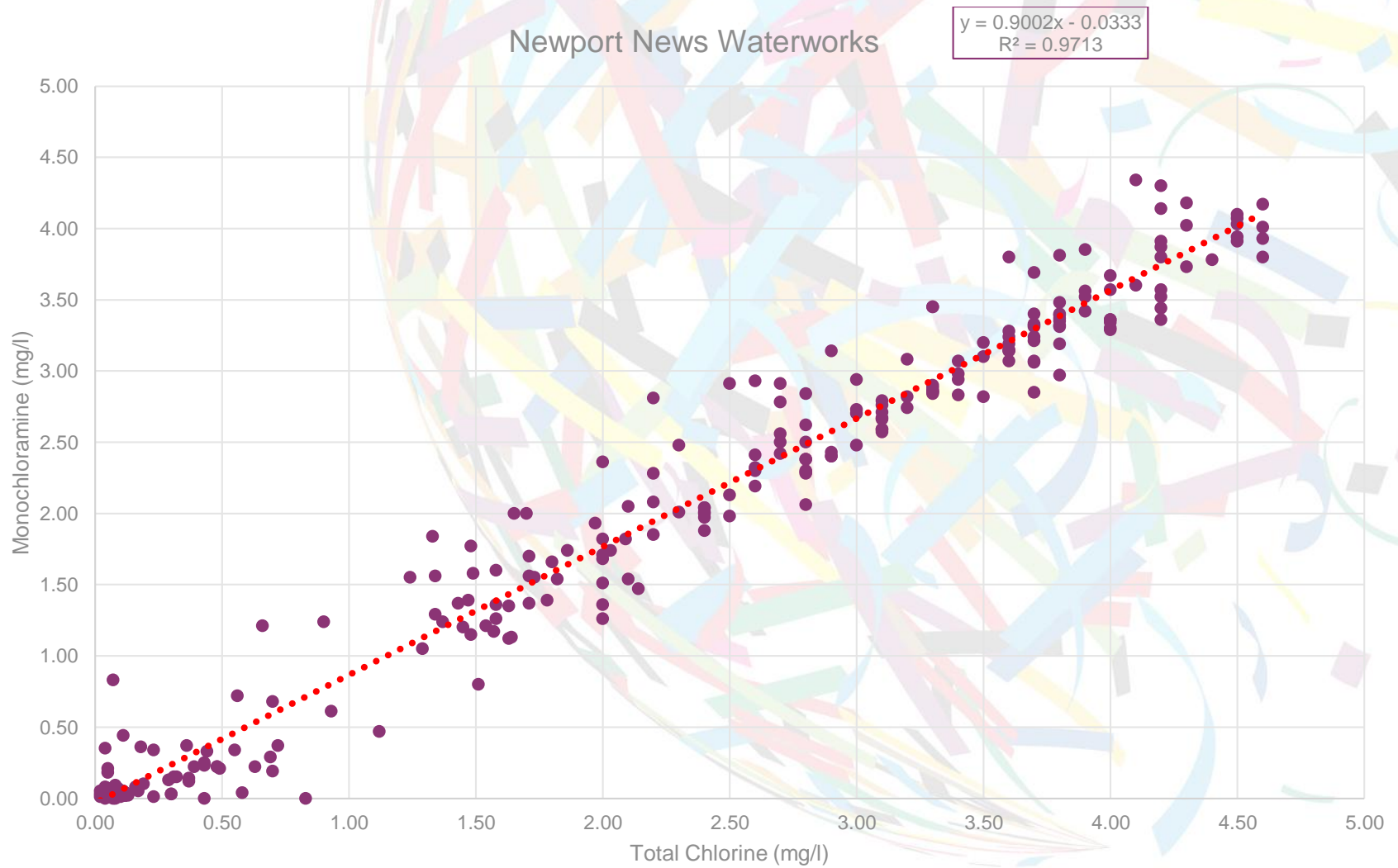


- Newport News Waterworks has been testing/using this kit since July 2015.
- Focus primarily on comparison of total chlorine and monochloramine readings.
- Range of instrument is 0.12 – 4.6 mg/l
- Claims to reduce inter-operator variability
- Method is not currently EPA approved for monochloramine.

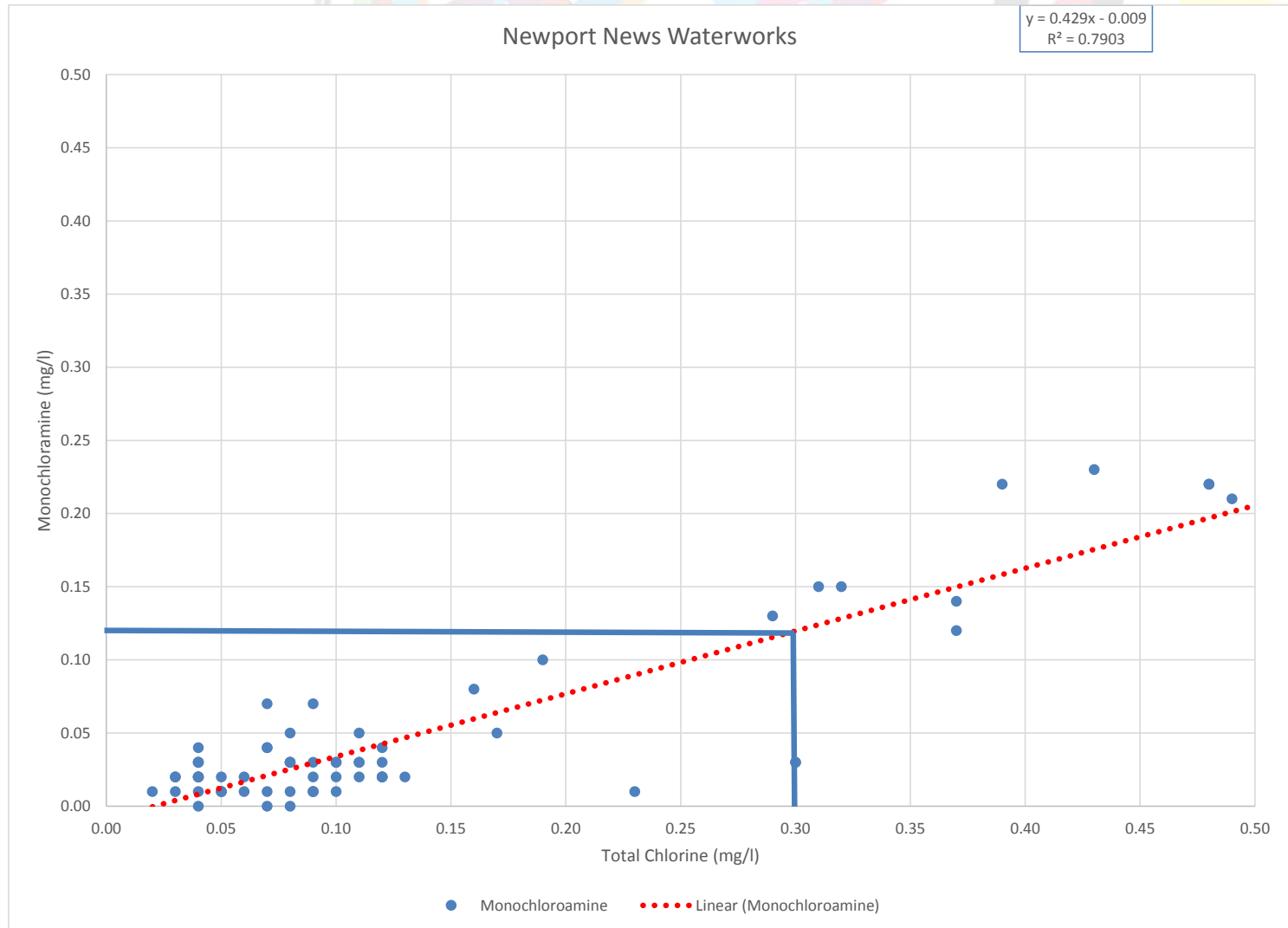
# SL1000 Portable Parallel Analyzer™ (PPA)



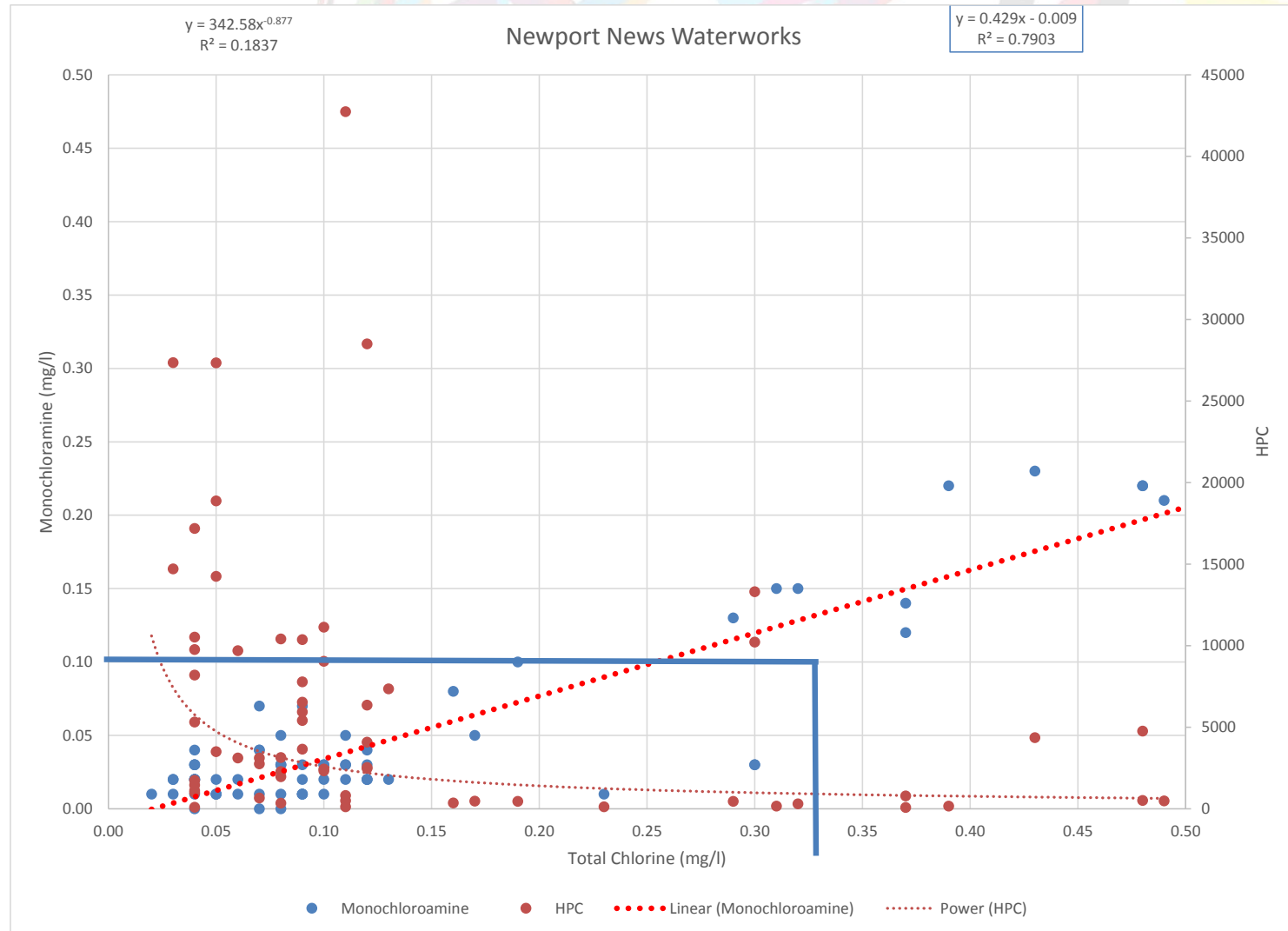
# Newport News Data



# Newport News Data low range



# Newport News Data low range

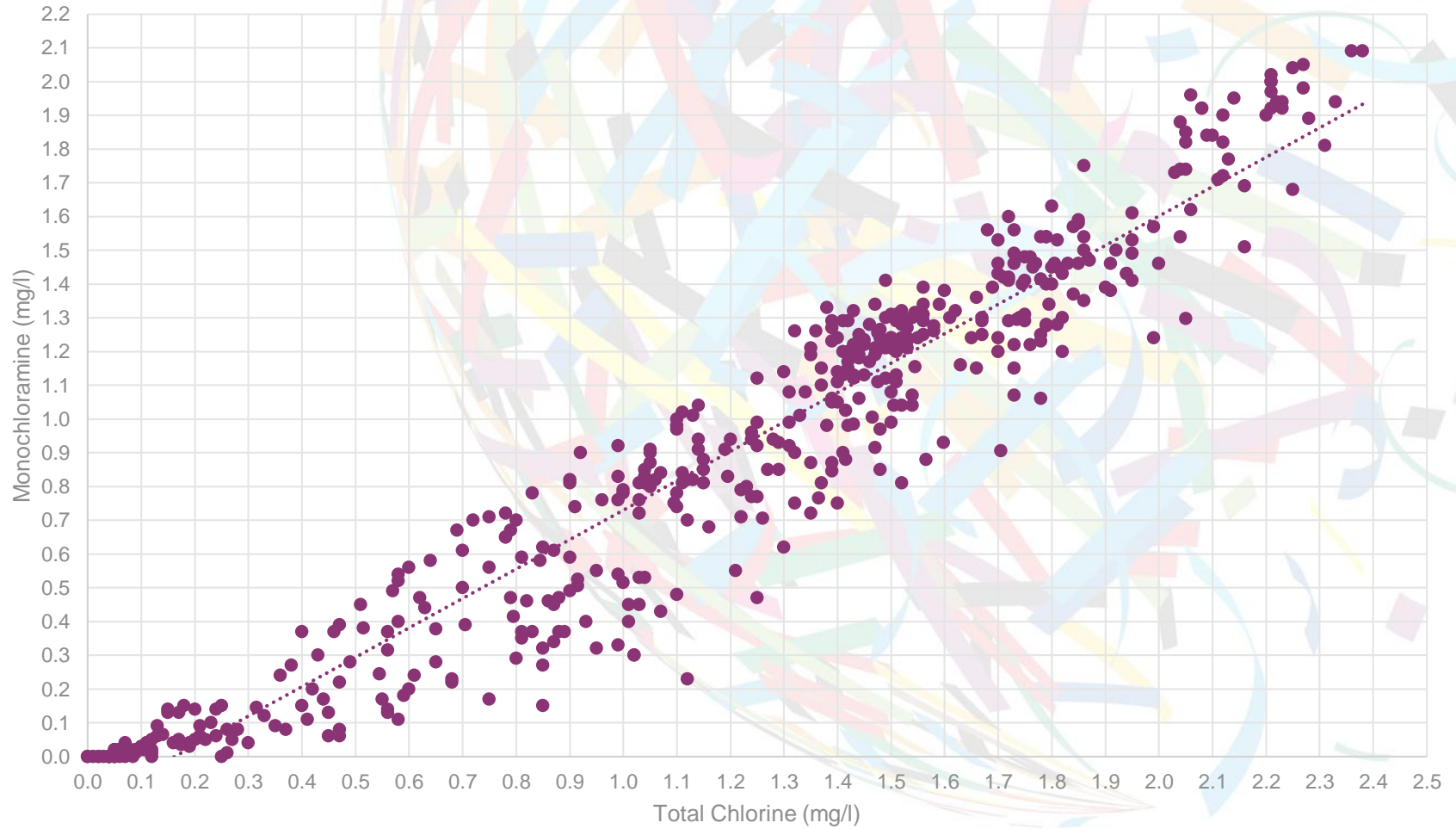


# Other Utilities Participation

- 3 other large utilities contributed free, total and monochloramine data.
  - Utility A used the amperometric method for determination of monochloramine and total chlorine
  - Utility B used the DPD method for total chlorine and indophenol method for monochloramine.
  - Utility C used the DPD method for total chlorine and indophenol method for monochloramine.

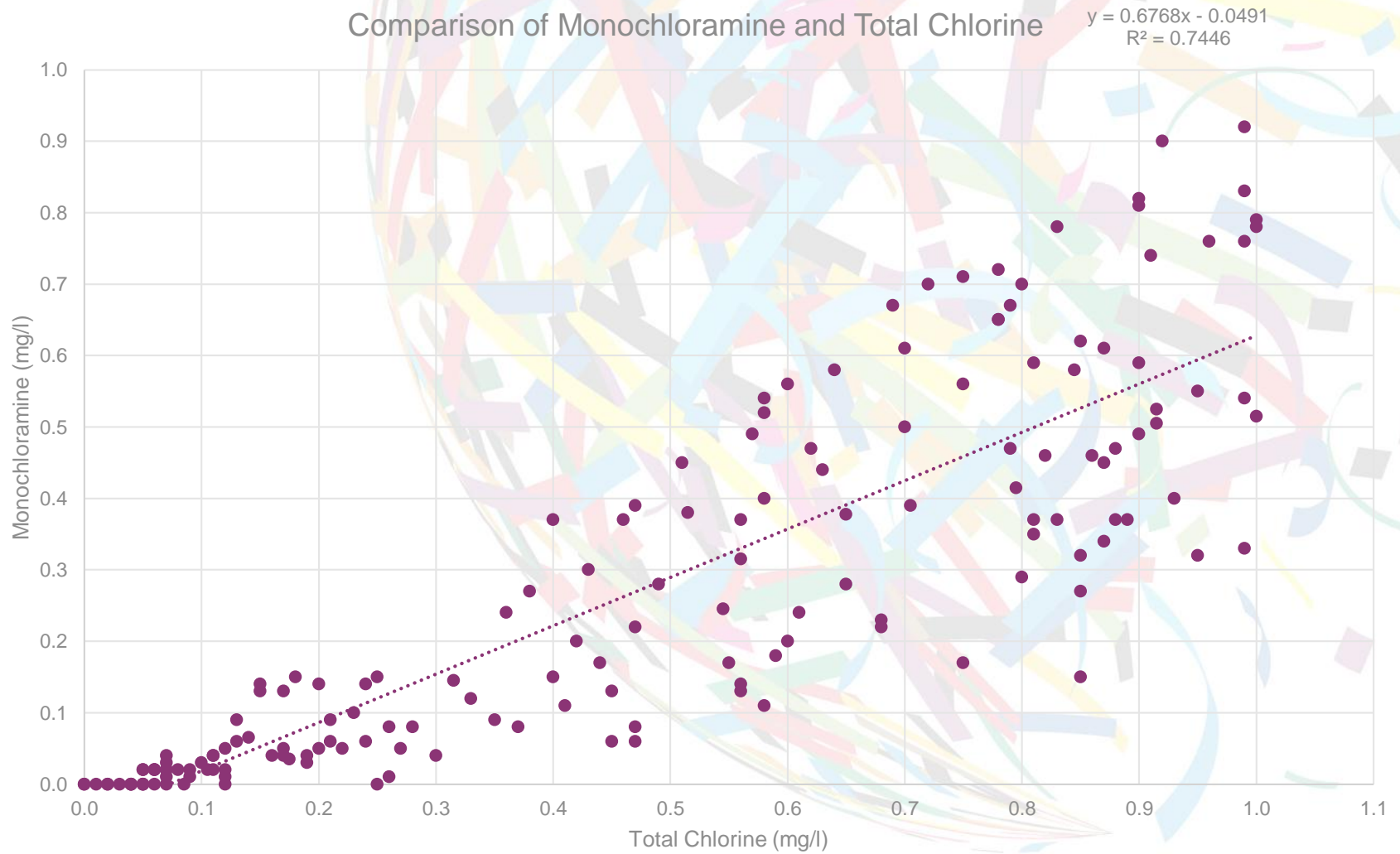
# Utility A

Comparison of Monochloramine and Total Chlorine  $y = 0.8715x - 0.1421$   
 $R^2 = 0.9248$

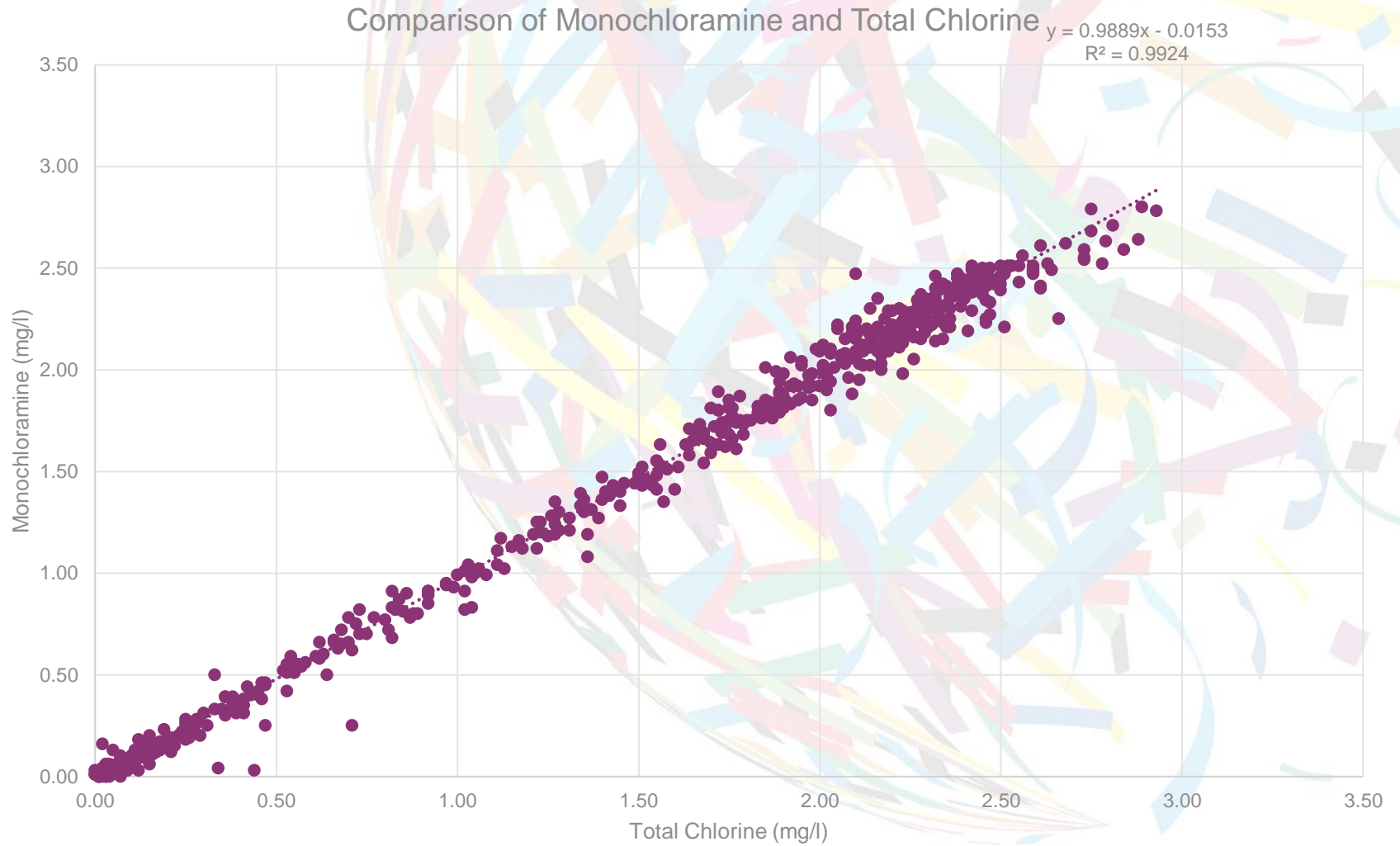


# Utility A

Comparison of Monochloramine and Total Chlorine



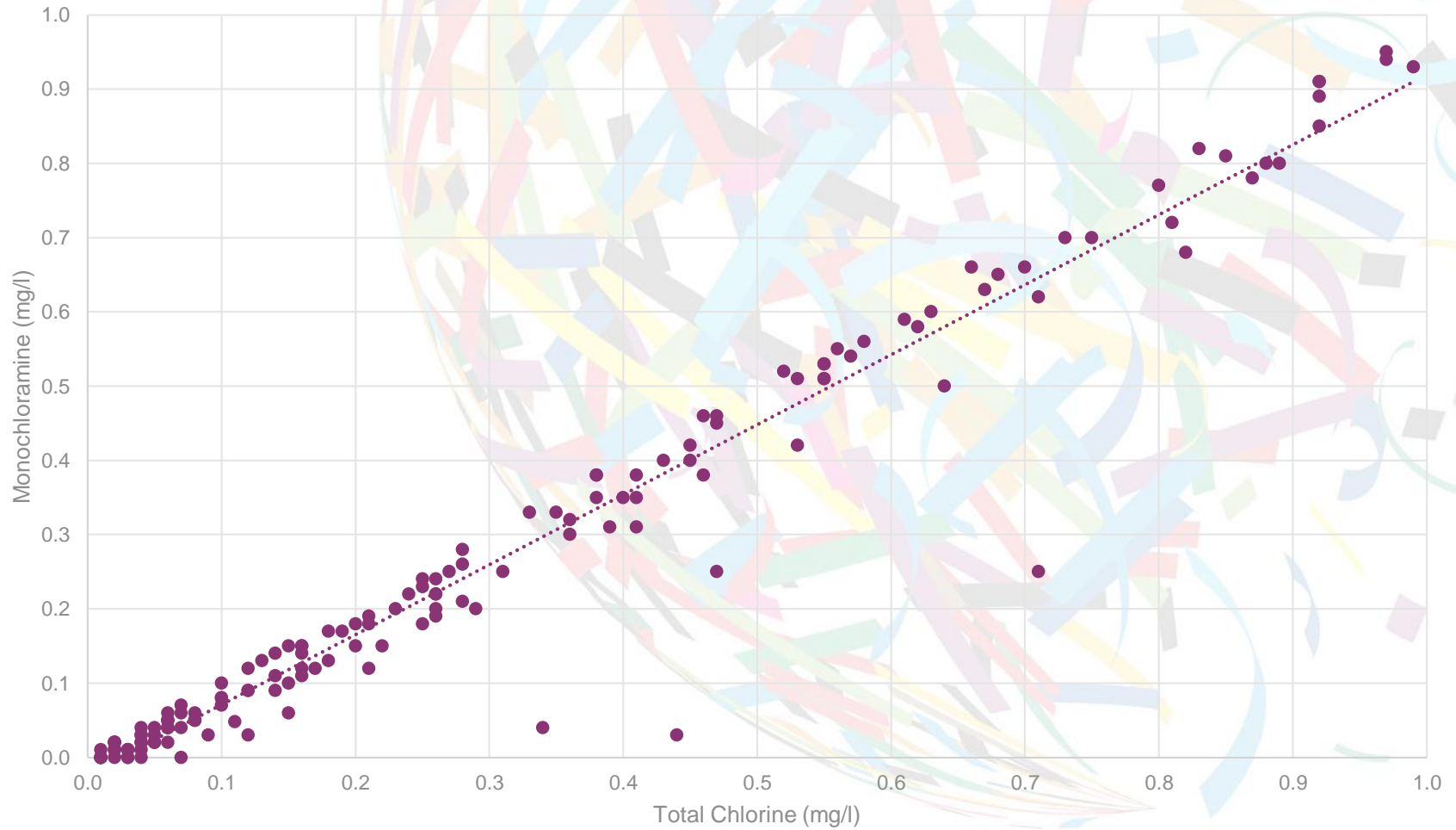
# Utility B



# Utility B

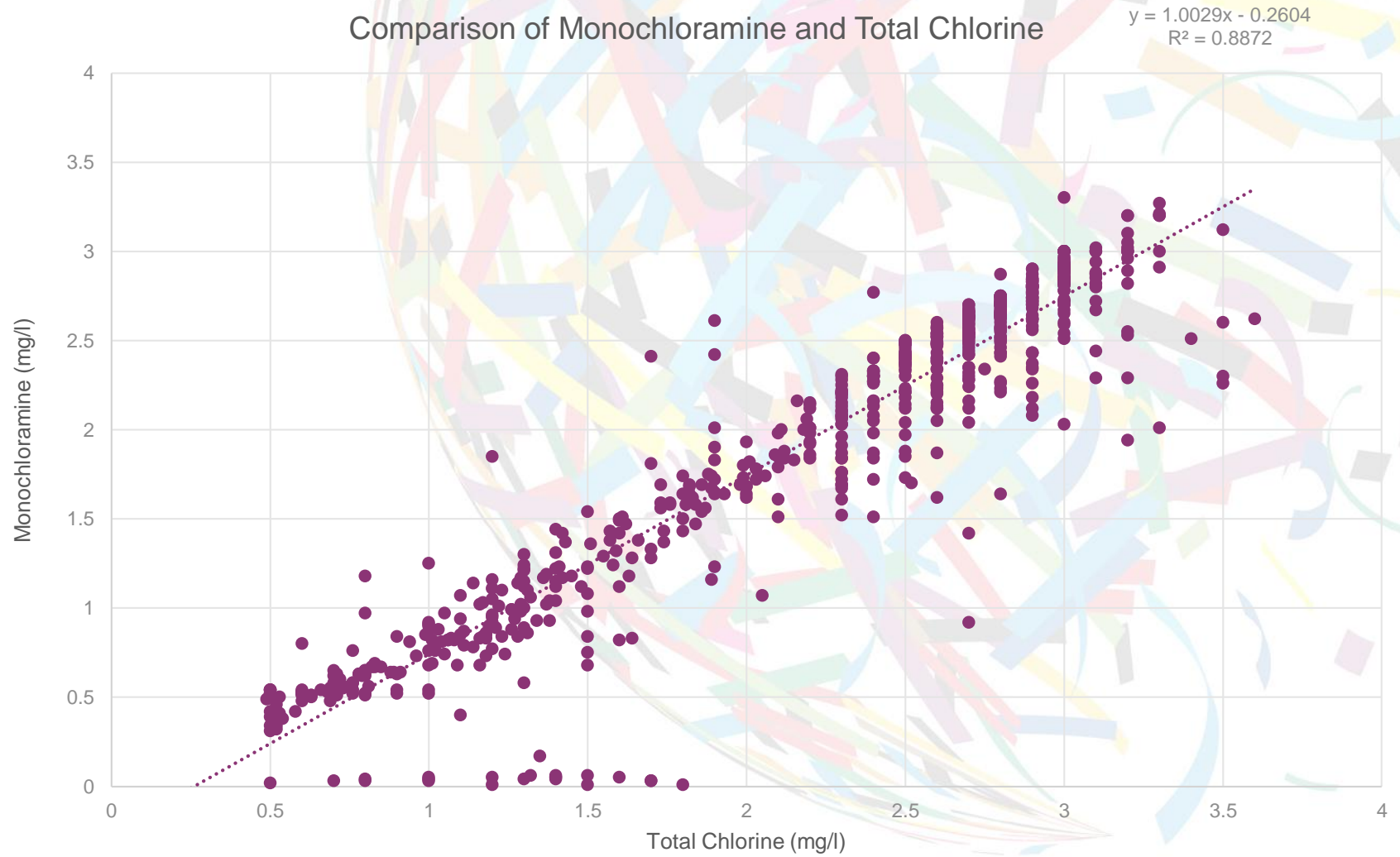
Comparison of Monochloramine and Total Chlorine

$$y = 0.9424x - 0.0231$$
$$R^2 = 0.9542$$



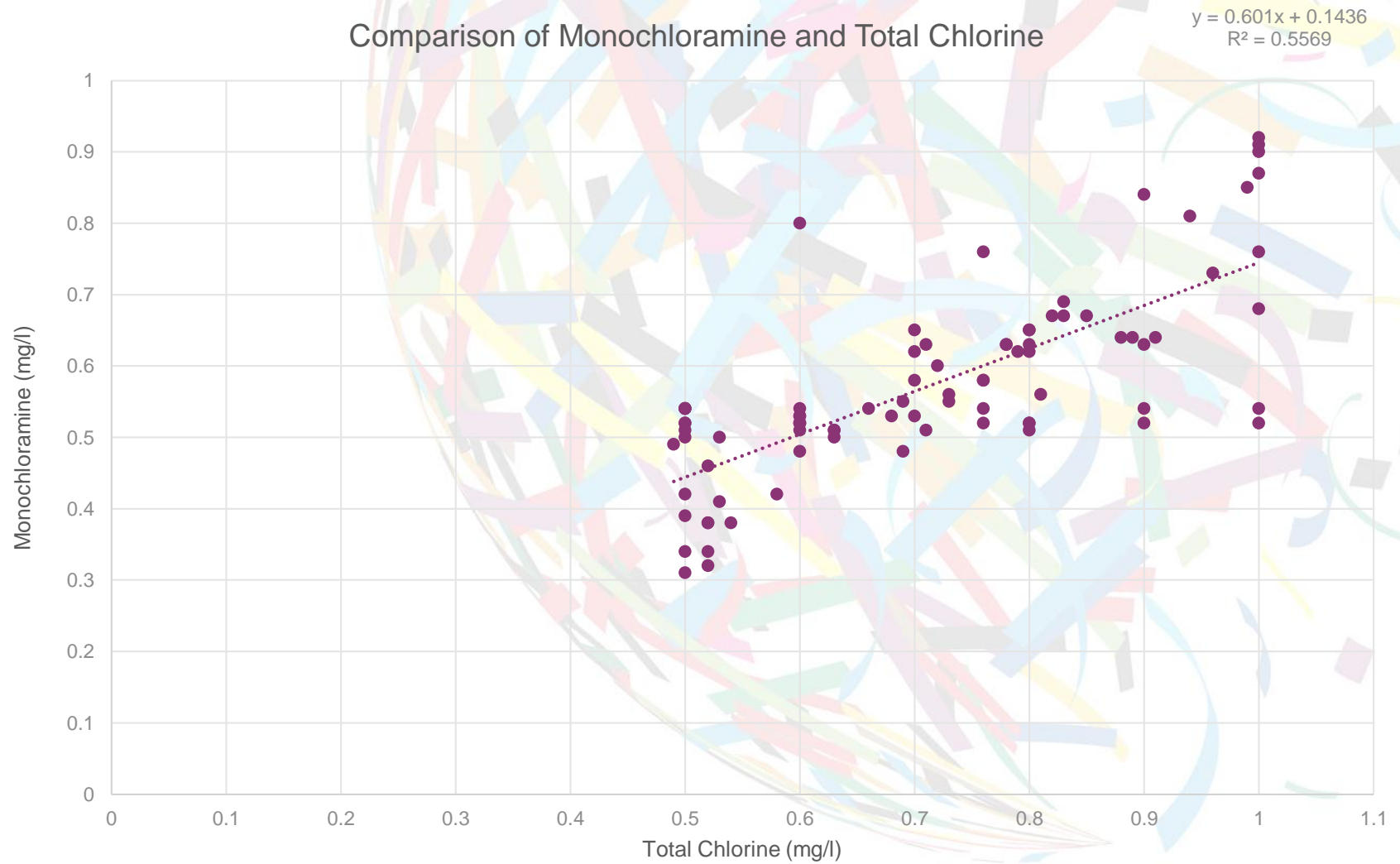
# Utility C

Comparison of Monochloramine and Total Chlorine

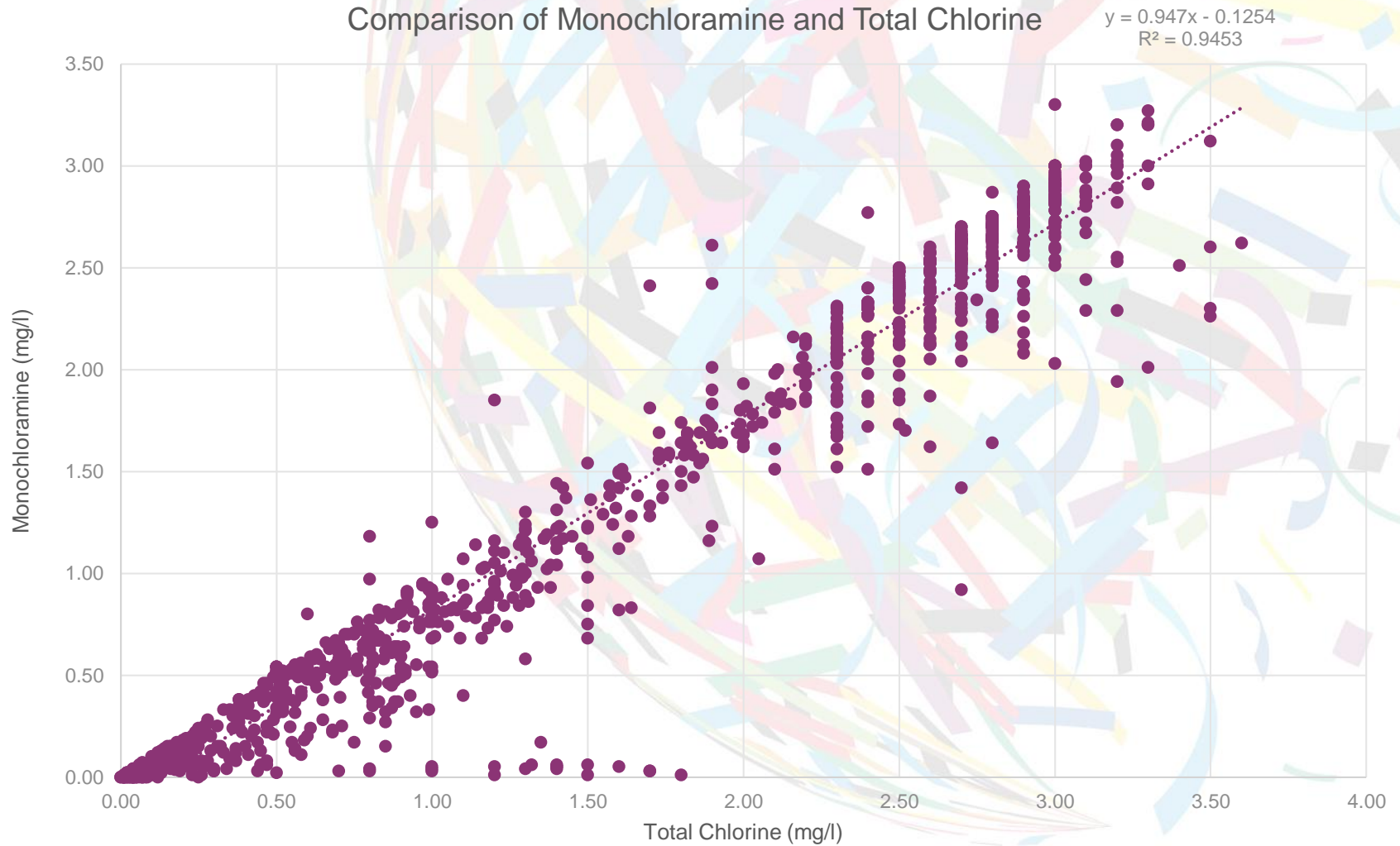


# Utility C

Comparison of Monochloramine and Total Chlorine



# All Four Utilities Pooled



# All Four Utilities Summary

<u>Utility</u>	<u>Monochloramine Concentration (mg/l)</u>	<u>Needed Total Chlorine Concentration (mg/l)</u>
Newport News Waterworks	0.12	0.30
A	0.12	0.25
B	0.12	0.15
C	0.12	0.38
All 4 Utilities Pooled	0.12	0.26

# Summary and Conclusions

- Four large utilities contributed data for a comparison of total chlorine and monochloramine concentration results.
  - Total chlorine was determined by the amperometric method for one utility and the other three used DPD
  - Monochloramine was determined by the amperometric method for one utility and the other three used indophenol method.
  - All data were from the utilities' distribution system, though not necessarily from the RTCR sites.

# Summary and Conclusions

- All four utilities showed a positive bias in the total chlorine results.
  - The positive bias ranged from a low average of 0.03 mg/l to a high average of 0.26 mg/l, with a weighted average for all of 0.14 mg/l.
- Whilst the SWTR requires a “detectable” total chlorine residual, the rule did not intend to include manganese and/or organic chloramines as a disinfectant.

# Summary and Conclusions

- The SWTR requires the reporting of total chlorine and the monochloramine test is not EPA-approved, so
  - Utilities should consider performing the total chlorine and monochloramine tests at their RTCR sites and others, especially where the total chlorine is less than 0.5 mg/l.
  - Attempt to manage the distribution system to maintain a detectable monochloramine residual at all RTCR sites.

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