

## **Water quality control measures in urban water distribution systems**

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### **Abstract**

The sodium hydroxide, sodium silicate, polyphosphate, and zinc-orthophosphate have been assessed for their effectiveness for corrosion inhibition in drinking water supply of the City of Thunder Bay. The data for each water quality parameter from control and test zones was assembled into two categories. The data pertaining to water samples collected during the first two weeks prior to the application of an inhibitor was assembled into the “before application category”. Likewise, the data pertaining to water samples collected during the last two weeks of the application of an inhibitor was assembled into the “Ending application category”. In each category, the grouping of data for the two weeks period provided statistical stability in the data set for subsequent analyses. After statistical screening of the data sets, these data sets were analyzed for variety test procedures. Based on the results of these tests, the polyphosphate, sodium hydroxide, and sodium silicate respectively were found to produce the greatest decrease (60%, 58%, and 45%) in lead levels, while zinc-orthophosphate caused an increase in lead level by 17%. The lead level in the control zone diminished gradually throughout the test. On the other hand, the sodium hydroxide, sodium silicate, polyphosphate, and zinc-orthophosphate respectively reduced copper level by 86%, 59%, 38%, and 4%. Again, the copper level in the control zone was found to diminish gradually throughout the test.

### **INTRODUCTION**

The issue of lead in drinking water has become a concern for many municipal water utilities. In 1989, the Guidelines for Canadian Drinking Water Quality, based on running-water samples, reduced the maximum allowable concentration of lead in drinking water from 0.5 mg/L to 0.01 mg/L. Preliminary investigations of water quality parameters in the water distribution network of the City of Thunder Bay indicated high levels of metals. These levels were attributed to corrosion of pipes in the distribution network due to slightly aggressive nature of the source water supply. The association of lead to mental disorder has been the unique factor that requires its level be kept within the stipulated guidelines. The lead contamination results from corrosion of lead-tin solders, lead piping, and lead-containing brasses in plumbing fixtures. A variety of corrosion inhibitors can be added to the drinking water to retard corrosion and the contaminant release. Irrespective of the well-characterized nature of various competing inhibitors, these must be evaluated in the specific environment of application. Since, the efficacy of a particular inhibitor is a function of specific water chemistry, the treatment procedures (i.e., the

application dosage and the operational sequencing etc.) for given water distribution network must be verified.

It appears that corrosion is strongly influenced by the seasonal changes in temperature and its attendant effects on water quality parameters. In this paper, several analyses of various water quality parameters have been conducted using statistical methods and bootstrap techniques. The results of these analyses are expected to provide a sound statistical basis for the assessment of competing inhibitors towards stabilization of the water quality in the water distribution network of the City of Thunder Bay.

## **STUDY AREA**

Corrosion is the deterioration of water supply pipes in residential, industrial, and commercial buildings, and within the water distribution network. A slightly aggressive water supply causes corrosion and eventually raises levels of metals in the drinking water supply network. In routine water sampling and testing program of the drinking water supply of the City of Thunder Bay, water samples from the Current River area of the water supply network were found to be slightly elevated in metals. The values of the lanellier-index were also found to be slightly negative, thus confirming the slightly aggressive and corrosive nature of the water supply in the Current River area. Under regulatory stipulations, the Ontario Ministry of the Environment (OME) recommended that a corrosion study be conducted to address the aggressive nature of the drinking water supply in the Current River area.

The City of Thunder Bay water distribution network in the Port-Arthur area is known as "North Ward". The Northward is divided into four water zones of which three have their own water distribution reservoirs. In the Current River area lies the smallest zone of these four zones. This smallest zone containing approximately 500 residential dwellings is referred to as Zone-1A. A 0.2 million gallons steel stand pipe reservoir and a 1.4 million gallons per day (mgd) booster pumping station provide the water pressure in this area.

The Current River area was chosen for the study because of the relatively low number of consumers and the non-existence of industrial water users. The boundary of Zone-1A cuts across the center of the Current River area. Further, the configuration of the water distribution network in Zone-1A is ideal for allowing the grouping of an equivalent number of dwellings in the test-zone and the control-zone. In each of the test and control zones, an equivalent number of dwellings with copper and lead connections were also selected. It is in this vein that a total of 25 dwellings with similar characteristics were selected in each of the test and control zones

## **APPLICATION SYSTEM FOR THE CORROSION INHIBITORS**

A description of the method used in application of various corrosion inhibitors is described elsewhere [(Ives et al (1999)]. Four chemical corrosion inhibitors were tested throughout the course of the study. These corrosion inhibitors were applied in a sequential order as follows: sodium hydroxide (caustic soda), sodium silicate, poly-

phosphate, and zinc-orthophosphate. Each corrosion inhibitors was tested over a three-month period. Each such application of a corrosion inhibitor was followed by a three month of “flush-out period”. To bring the overlap effects of inhibitors (which may arise due to their sequential application) to a minimum; a “flush- out period” was considered extremely important to allow for the corrosion levels to return to pre-additive conditions.

**Table 1. Summary of 90% values of Copper using Bootstrap methods (1000 samples).**

Analysis of Data collected in the Week-1 and Week-2	Case A: Test Zone											
	Type of Corrosion Inhibitor Treatment											
	Caustic Soda			Sodium Silicate			Polyphosphate			Zinc Orthophosphate		
	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv
Before the initiation of a Treatment	298.3	74.1	0.25	447.5	73.2	0.16	310.3	69.1	0.22	136.9	10.5	0.08
After the completion of a Treatment	41.1	4.1	0.10	183.8	40.7	0.22	191.8	31.3	0.16	131.7	17.3	0.13
Percent Change	-86.2	-	-60.0	-58.9	-	37.5	-38.2	-	-27.3	-3.8	-	62.5
Analysis of Data collected in the Week-1 and Week-2	Case B: Control Zone											
	Type of Corrosion Inhibitor Treatment											
	Caustic Soda			Sodium Silicate			Polyphosphate			Zinc-Orthophosphate		
	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv
Before the initiation of a Treatment	164.5	14.3	0.09	306.1	78.2	0.26	209.1	73.3	0.35	131.0	51.2	0.39
After the completion of a Treatment	143.9	15.7	0.11	278.4	96.2	0.36	156.3	22.4	0.14	117.8	11.7	0.10
Percent Change	-12.5	-	22.2	-9.1	-	38.5	-25.3	-	-60.0	-10.1	-	-74.4

Note-1: The values of the mean and the standard deviations are in  $\mu\text{g/l}$ .

Note-2: Negative and positive values of the percent-change are respectively indicative of the effectiveness or the in-effectiveness of a particular corrosion inhibitor either in the Control zone or the Test zone.

The corrosion study program was initiated in summer of 1996 with the application of the first chemical corrosion inhibitor in September of that year, and was successfully completed in December of 1998. The sequential order in which the corrosion inhibitors were tested was sodium hydroxide, sodium silicate, poly-phosphate, and zinc-orthophosphate. It is noted that an effort was made to ensure, on the average, that the characteristics of dwellings in the test and control zones were similar. However, variations in these characteristics in the test zone and control zone were apparent due to dwelling size, year of construction, materials and methods used for water pipes in dwellings and in water distribution network in this area. Further, the effects arising due to seasonal changes, especially those attributable to variations in water temperature at the source and throughout the water distribution system require careful consideration and analysis.

## DATA COLLECTION AND ANALYSES

In each of the test and control zones, 25 volunteers collected four water samples for each of the four chemical corrosion inhibitors. Two of these four samples were collected as follows. Sample-one and sample-two were respectively collected two-week prior and one-week prior to initiation of the application of a particular inhibitor. Sample-three and sample-four were respectively collected two-week and one-week prior to ending (i.e., completion) of the application of a particular corrosion inhibitor. Each sample was preserved according to OME guidelines and was forwarded to OME laboratories for further chemical analyses. To ensure that the correct concentrations of the inhibitors were maintained during the study period, samples were also taken on a daily basis at three locations in the test zone.

Water samples at designated locations (i.e., 25 dwellings in each test and control zones) were collected throughout the study period. To capture the essential characteristics of water quality in the test and control zones, two weeks prior to initiation, and two weeks prior to completion, of the application a particular corrosion inhibitor, an intensive water-sampling program was conducted. These water samples were analyzed at the MOE laboratories for a variety of water quality parameters [Panu, 2000].

## STATISTICAL DATA ANALYSES

For the test and control zones, the data on various water quality parameters was assembled. The data for each water quality parameter (aluminum, zinc, copper, lead, iron, and manganese) from these zones was assembled into two categories. The data pertaining to water samples collected during the first two weeks prior to initiation of the application of an inhibitor were assembled into the “before-application-category”. Likewise, the data pertaining to water samples collected during the two weeks prior to completion of the application of an inhibitor were assembled into the “ending-application category”. Preliminary investigations on various aspects of the data corresponding to each category revealed that for statistical stability it is necessary to group the data for the two weeks period into one group of data. For each corrosion inhibitor, as a result, data on various water quality parameters was organized into two categories, such as the “before-application-category” and the “ending-application category”. The data sets thus organized formed the basis of subsequent analyses.

### Statistical Screening of Data Sets

A statistical screening of the data sets was carried out to assess the presence or absence of “high and/or low outliers”. A number of statistical tests for outliers were conducted based on such methods as: the U.S. Water Resources Council method, the Inter Quartile Range method, the mean+ $zS$ , and the Cumulative Frequency Plot method. A description of these methods and their computation and/or interpretation scenarios of test results can be found elsewhere [Panu (2000)]. In general, low outliers were found to be insignificant except in some cases of the lead water quality parameter. The data sets were not modified for the low-outliers. However, the data sets were modified when a number of tests attested the

presence of one or more outliers in a particular data set. Panu (2000) provides a summary of modified data sets.

**Table 2. Summary of 90% values of Lead using Bootstrap methods (1000 samples).**

Analysis of Data collected in the Week-1 and Week-2	Case A: Test Zone											
	Type of Corrosion Inhibitor Treatment											
	Caustic Soda			Sodium Silicate			Polyphosphate			Zinc Orthophosphate		
	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv
Before the initiation of a Treatment	209	4.34	0.21	329	7.8	0.24	203	5.56	0.27	9.33	1.51	0.16
After the completion of a Treatment	7.49	1.02	0.14	179	4.3	0.24	2.3	0.74	0.32	12.1	3.04	0.25
Percent Change	-64.2		-33.3	-45.6	-	0.00	-88.7	-	18.5	29.7	-	56.3
Analysis of Data collected in the Week-1 and Week-2	Case B: Control Zone											
	Type of Corrosion Inhibitor Treatment											
	Caustic Soda			Sodium Silicate			Polyphosphate			Zinc Orthophosphate		
	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv	Mean	S.D.	Cv
Before the initiation of a Treatment	44.5	6.59	0.15	38.5	4.99	0.13	42.8	6.91	0.16	33.9	5.16	0.15
After the completion of a Treatment	41.5	6.8	0.16	38.7	3.87	0.10	30.6	6.35	0.21	38.2	5.68	0.15
Percent Change	-6.7	-	6.7	-0.52	-	-23.1	-28.5	-	31.3	12.7	-	0.00

Note-1: The values of the mean and the standard deviations are in  $\mu\text{g/l}$ .

Note-2: Negative and positive values of the percent-change are respectively indicative of the effectiveness or the in-effectiveness of a particular corrosion inhibitor either in the Control zone or the Test zone.

### Data Simulations Based on Bootstrap Procedures

To assess the relative efficacy of various corrosion inhibitors, a bootstrap program was developed. This program provided simulated samples of a given sample data. Through initial investigations and iterative experimentation, it was found that one need to simulate more than 600 samples to ensure the statistical stability of the mean, variance, coefficients of the skewness, kurtosis, and variation. Therefore, it was deemed imperative to develop a bootstrap program capable of simulating 1000 samples. The values of the average (i.e., the mean), standard deviation (S.D.), and percentiles at 50%, 90% and 95% were obtained for each of the simulated samples. These 1000 values corresponding to the 90 percentile were subsequently considered to form a sample of which the average and standard deviation were computed. The values of the average and standard deviation thus computed were considered to provide stable statistical parameters for further analyses.

In case of a particular water quality parameter (Tables 1 and 2), the values of the average and the standard deviation were thus computed for each of the four corrosion inhibitors under two “before-application” and “ending-application” categories. These tables also

contain values of the coefficient of variation (standard deviation/average) which is a measure of variability irrespective of the magnitude of the data values. (The coefficient of variation is a dimensionless measure of variability in a data set).

**Table 3. Summary of 90% values of Copper and Lead Using Bootstrap methods (1000 samples).**

Analysis of Data Collected in the Week-1 and Week-2	Types of Corrosion Inhibitor Treatment							
	Caustic Soda		Sodium Silicate		Polyphosphate		Zinc Orthophosphate	
	Mean	C <sub>v</sub>	Mean	C <sub>v</sub>	Mean	C <sub>v</sub>	Mean	C <sub>v</sub>
Percent Change	Copper (Test Zone)							
	-86.2	-60.0	-58.9	37.5	-38.2	-27.3	-3.8	62.5
Percent Change	Copper (Control Zone)							
	-12.5	22.2	-9.1	38.5	-25.3	-60.0	-10.1	-74.4
Net Change (%)	-73.7	-37.8	-49.8	-10.0	-12.9	32.7	13.9	136.9
Percent Change	Lead (Test Zone)							
	-64.2	-33.3	-45.6	0.0	-88.7	18.5	29.7	56.3
Percent Change	Lead (Control Zone)							
	-6.7	6.7	-0.52	-23.1	-28.5	31.3	12.7	0.0
Net Change (%)	-57.5	-40.0	-45.1	23.1	-60.2	-12.8	17.0	56.3

Note-1: Negative and positive values of the percent-change are respectively indicative of the effectiveness or the in-effectiveness of a particular corrosion inhibitor either in the Control zone or the Test zone.

Note-2: Negative values of the net-percent-change are indicative of the absolute-effectiveness of a particular corrosion inhibitor in relation to the prevalent conditions in the Control zone due to non-application of a particular corrosion inhibitor.

## RESULTS AND DISCUSSION

The average value corresponding to the 90 percentile was obtained to access the capability of a particular corrosion inhibitor to contain the desired limit of the water quality parameter. Such desired limits are stated in the Canadian Drinking Water Standard and also specified in the Ontario Drinking Water Objectives. The values of percent change of a parameter in these tables were computed as follows.

$$\text{Percent Change} = \frac{[\text{Value "Before the Treatment"} - \text{Value at "Ending the Treatment"}]}{\text{Value Before the Treatment}} * 100.$$

The magnitude of a negative value of percent-change indicates the degree of effectiveness of a particular corrosion inhibitor. On the other hand, the magnitude of a positive value of the percent-change indicates the degree of in-effectiveness of a particular corrosion inhibitor. For example, a value of + 29.7 (Table 2) for the zinc-orthophosphate in case of the lead indicates that this corrosion inhibitor is not only ineffective but rather enhances the leaching of lead in drinking water supply.

From the results (Table 1), it is apparent that caustic soda is the most effective inhibitor in reducing the levels of copper. A corresponding reduction in value of the coefficient of variation (Cv) is indicative of the reliability of this inhibitor. Although, sodium silicate is found to be the second most effective inhibitor but a positive value of the Cv indicates

that the data variability has increased due to application of this corrosion inhibitor. The third effective corrosion inhibitor found to be the polyphosphate with an added advantage of being more reliable in its effectiveness since its value of the Cv is negative. However, zinc-orthophosphate was found to be nearly ineffective in reducing the copper levels in drinking water supply.

The results (Table 2) suggest that although the most effective corrosion inhibitor is the polyphosphate but has a positive value of the Cv. In other words, this corrosion inhibitor is less reliable. Caustic soda is again found to be an effective corrosion inhibitor with higher degree of reliability than the polyphosphate corrosion inhibitor. The sodium silicate is the third most effective corrosion inhibitor. The zinc-orthophosphate was found to rather enhance the leaching of lead and thus causing the lead levels to rise in drinking water supply.

In view of the results obtained for the control zone, which is considered to be the mirror image representative of conditions in the test zone, had there been no application of corrosion inhibitors. Table 3 summarizes the overall changes in the average-value that can be interpreted from the results obtained in the test zone. Such changes are computed as net-percent-change for a water quality parameter as follows.

**Net-percent-change** = [(Percent-change in test zone) - (Percent- Change in control zone)]\*100.

A summary of the net-percent-change in the average-value for copper and lead, and for the four chemical corrosion inhibitors is provided in Table 3. Similarly, the net-percent-change for the coefficient of variation (Cv) is also summarized in this table. It is apparently clear from this table that the overall best effective corrosion inhibitor for copper and lead is the caustic soda. The corrosion inhibitor polyphosphate does exhibit a slight advantage over the caustic soda for the inhibiting lead levels. However, for a consistent and reliable effectiveness and performance for corrosion inhibition in drinking water supply, sodium hydroxide (caustic soda) is the best choice. The corrosion inhibitor polyphosphate is a reasonable alternative but was found to be relatively less reliable in effectiveness and performance. The corrosion inhibitor sodium silicate is the third best choice with a significantly reduced reliability in effectiveness and performance. The corrosion inhibitor zinc-orthophosphate should not be considered.

## CONCLUSIONS

The four corrosion inhibitors tested in this study, the polyphosphate, sodium hydroxide (caustic soda), and sodium silicate respectively were found to produce the greatest decrease (60%, 58%, and 45%) in lead levels, while zinc-orthophosphate caused an increase in lead level by 17%. The lead levels in the control zone tend to diminish gradually throughout the study period. On the other hand, the sodium hydroxide (caustic soda), sodium silicate, polyphosphate, and zinc-orthophosphate respectively reduced copper levels by 86%, 59%, 38%, and 4%. Again, the copper levels in the control zone tend to diminish gradually throughout the study period.

The corrosion inhibitor polyphosphate exhibits a slight advantage over the caustic soda for the inhibiting lead levels. For a consistent and reliable effectiveness and performance in corrosion inhibition, sodium hydroxide (caustic soda) represents the best choice. The corrosion inhibitor polyphosphate is a reasonable alternative but in view of effectiveness and performance, it was found to be relatively less reliable than the sodium hydroxide. The corrosion inhibitor sodium silicate represents the third best choice with a significantly reduced reliability both in effectiveness and performance. The corrosion inhibitor zinc-orthophosphate should not be considered as a corrosion inhibitor in the City of Thunder Bay water supply network.

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