BROWN AND CALDWELL

Technical Memorandum

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Prepared for: City of Boulder, Littleton/Englewood WWTP, and Xcel Energy

Project Title: Comparison of Paired Total Recoverable and Potentially Dissolved Metals Discharge Data

Project No: Multiple

DRAFT Technical Memorandum No. 1

Subject: Comparison of Paired Total Recoverable and Potentially Dissolved Metals Discharge Data

Date: October 30, 2007

To: Reg. 61 Workgroup

From: Sarah Reeves, Project Manager

Prepared by: _____

Sarah Reeves, Project Manager

Reviewed by: _____

Michelle Wind, QA/QC

Limitations:

This document was prepared solely for the City of Boulder, Littleton/Englewood WWTP, and Xcel Energy in accordance with professional standards at the time the services were performed. This document is governed by the specific scope of work authorized by the City of Boulder, Littleton/Englewood WWTP, and Xcel Energy; it is not intended to be relied upon by any other party except for regulatory authorities contemplated by the scope of work. We have relied on information or instructions provided by the City of Boulder, Littleton/Englewood WWTP, and Xcel Energy and other parties and, unless otherwise expressly indicated, have made no independent investigation as to the validity, completeness, or accuracy of such information.

1. BACKGROUND

The Regulation 61 Workgroup was developed to discuss and resolve conflicting language and consider other changes to the Colorado Discharge Permit System Regulation (Reg. 61). Existing language in the Code of Federal Regulations (40 CFR 122.45(c)) requires permit limits for metals to be expressed as total recoverable. Current Reg. 61 language (61.8(2)(b)(vii)) requires permit limits for metals to be expressed as potentially dissolved, with allowances for reporting as dissolved or total recoverable if certain conditions are met by the discharger. The Water Quality Control Division (Division) expressed a desire to make Reg. 61 language match the 40 CFR 122 language and proposed to make the change in the regulation using a one to one relationship between potentially dissolved and total recoverable metals (as had been previously done between dissolved and potentially dissolved metals). A number of workgroup participants were concerned with this assumption and with the impact that this change in discharge permit limits would have on the state's dischargers. As a result, several dischargers (City of Boulder, Centennial W&S District, Littleton/Englewood WWTP, City of Pueblo, and Xcel Energy) provided metals discharge data to Brown and Caldwell to perform a comparison.

2. POTENTIALLY DISSOLVED VERSUS TOTAL RECOVERABLE

In order to better understand whether there is a difference between potentially dissolved and total recoverable metals in wastewater discharges, Brown and Caldwell looked at paired data collected from 1999 through 2006 from a number of wastewater sources, including:

- City of Boulder - Copper
- Centennial W&S District – Copper
- Littleton/Englewood Wastewater Treatment Plant – Cadmium, Copper, Lead, Molybdenum, Nickel, Selenium, Zinc
- City of Pueblo – Arsenic, Cadmium, Chromium, Copper, Lead, Manganese, Nickel, Selenium, Silver
- Xcel Energy – Iron

In order to understand the relationship between potentially dissolved and total recoverable metals, the paired data were plotted, the ratio of potentially dissolved to total recoverable was graphed, and box plots of the data were developed (See Attachment A). Several observations can be made about these graphs:

- The relationship between potentially dissolved and total recoverable results varies from metal to metal.
- The relationship between potentially dissolved and total recoverable results varies from discharger to discharger (see the copper results that are common to most dischargers).
- The ratio of potentially dissolved to total recoverable concentrations ranges from 0.2 to 1.
- The box plots show that the distributions of potentially dissolved and total recoverable concentrations overlap for some constituents and don't for others, which is a visual measure of whether they are statistically different populations.

We also performed the Mann-Whitney test, a nonparametric test that compares two samples to see if they are different (whether or not they come from the same population). The results of the statistical test are provided in Table 1.

Table 1. Mann-Whitney Test Results (α = 0.05)			
Discharger	**Constituent**	**Mann-Whitney p-value**	**Interpretation**
City of Boulder	Copper	0.4168	Medians (populations) are equal
Centennial W&S District	Copper	0.0731	Medians (populations) are equal
Littleton/Englewood WWTP	Cadmium	NA	Not able to be calculated*
Littleton/Englewood WWTP	Copper	0.0765	Medians (populations) are equal
Littleton/Englewood WWTP	Lead	NA	Not able to be calculated*
Littleton/Englewood WWTP	Molybdenum	0.4678	Medians (populations) are equal
Littleton/Englewood WWTP	Nickel	0.0545	Medians (populations) are equal
Littleton/Englewood WWTP	Selenium	0.3005	Medians (populations) are equal
Littleton/Englewood WWTP	Zinc	0.1437	Medians (populations) are equal
City of Pueblo	Arsenic	0.4034	Medians (populations) are equal
City of Pueblo	Cadmium	0.4529	Medians (populations) are equal
City of Pueblo	Chromium	0.0065	Medians (populations) are NOT equal
City of Pueblo	Copper	0.5907	Medians (populations) are equal
City of Pueblo	Lead	0.2332	Medians (populations) are equal
City of Pueblo	Manganese	0.0207	Medians (populations) are NOT equal
City of Pueblo	Nickel	0.1253	Medians (populations) are equal
City of Pueblo	Selenium	0.0029	Medians (populations) are NOT equal
City of Pueblo	Silver	0.007	Medians (populations) are NOT equal
Xcel Energy	Iron	0.0000	Medians (populations) are NOT equal

*The Mann-Whitney could not be calculated, probably because of lack of data.

The results of the Mann-Whitney test show that there is a significant difference between potentially dissolved and total recoverable results for the City of Pueblo's silver, chromium, manganese, and selenium results and Xcel Energy's iron results.

This data review was based on five data sets, with two data set providing sufficient data on more than two constituents. While paired data on all regulated metals are obviously scarce, the data that we have been able to review show that there are differences between potentially dissolved and total recoverable results on at least some metals. The review also shows that these differences appear to be site specific.

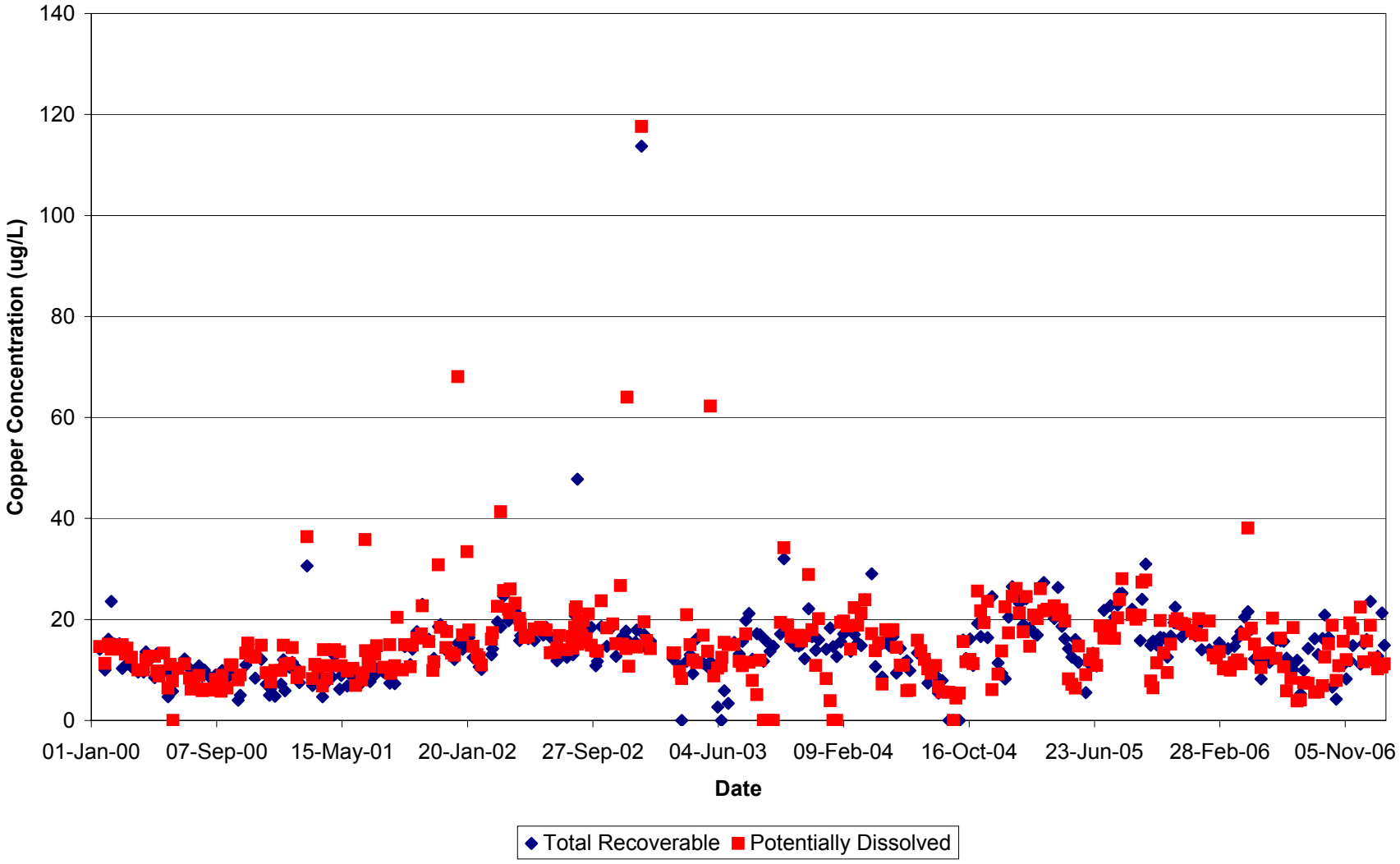
ATTACHMENT A

Potentially Dissolved and Total Recoverable Plots

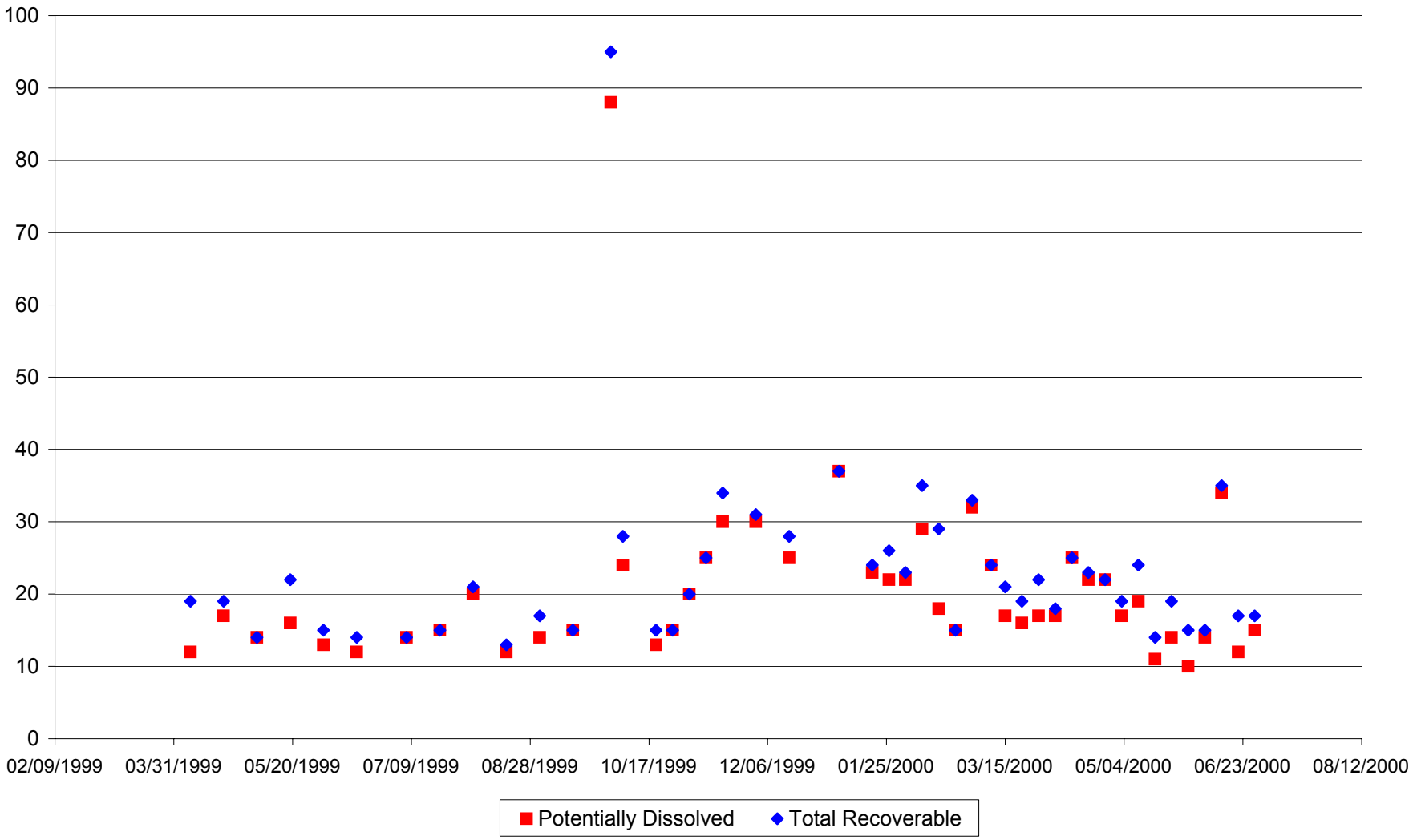
Ratio of Potentially Dissolved to Total Recoverable

Box Plots

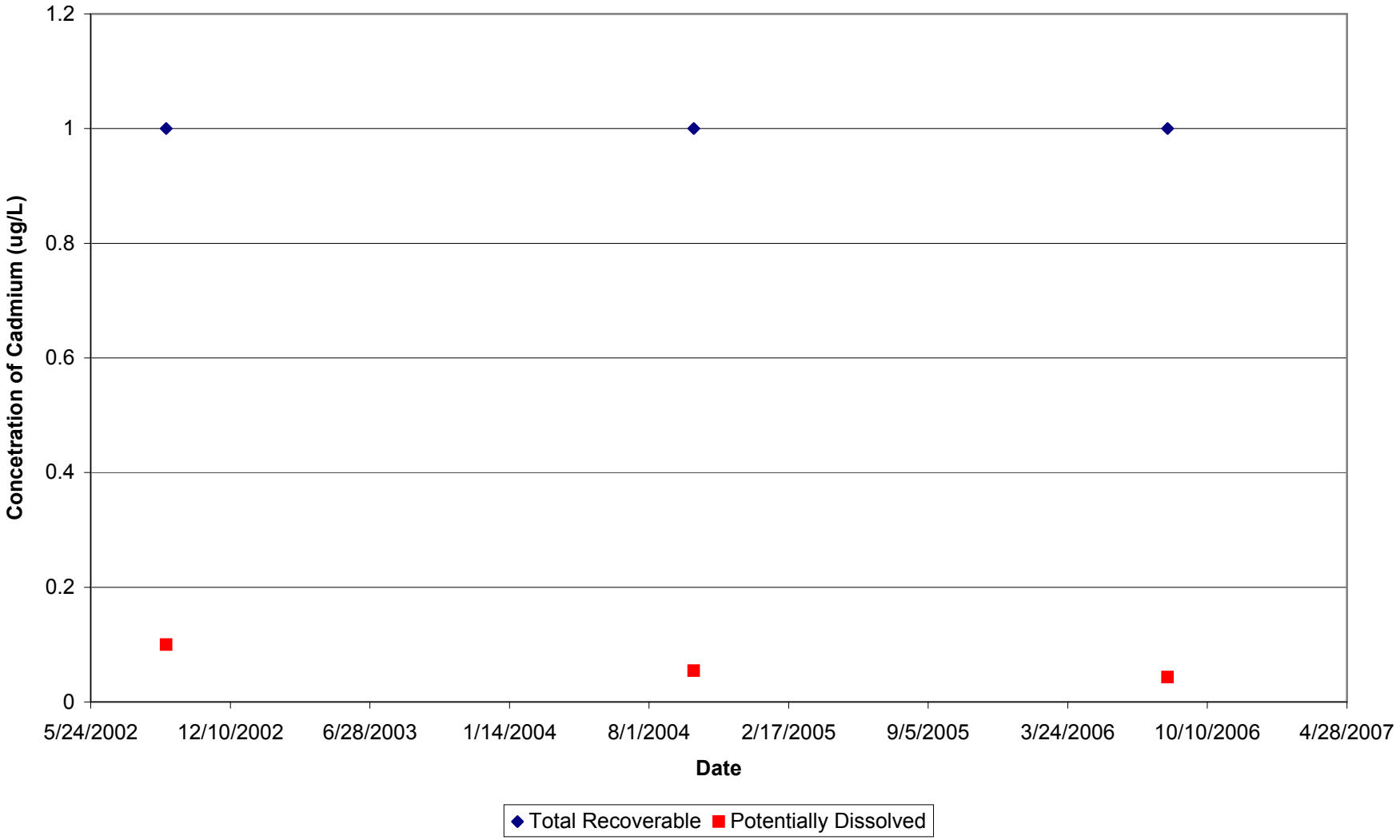
Comparison of Measured Total Recoverable and Potentially Dissolved Copper Concentrations in the City of Boulder WWTP Effluent



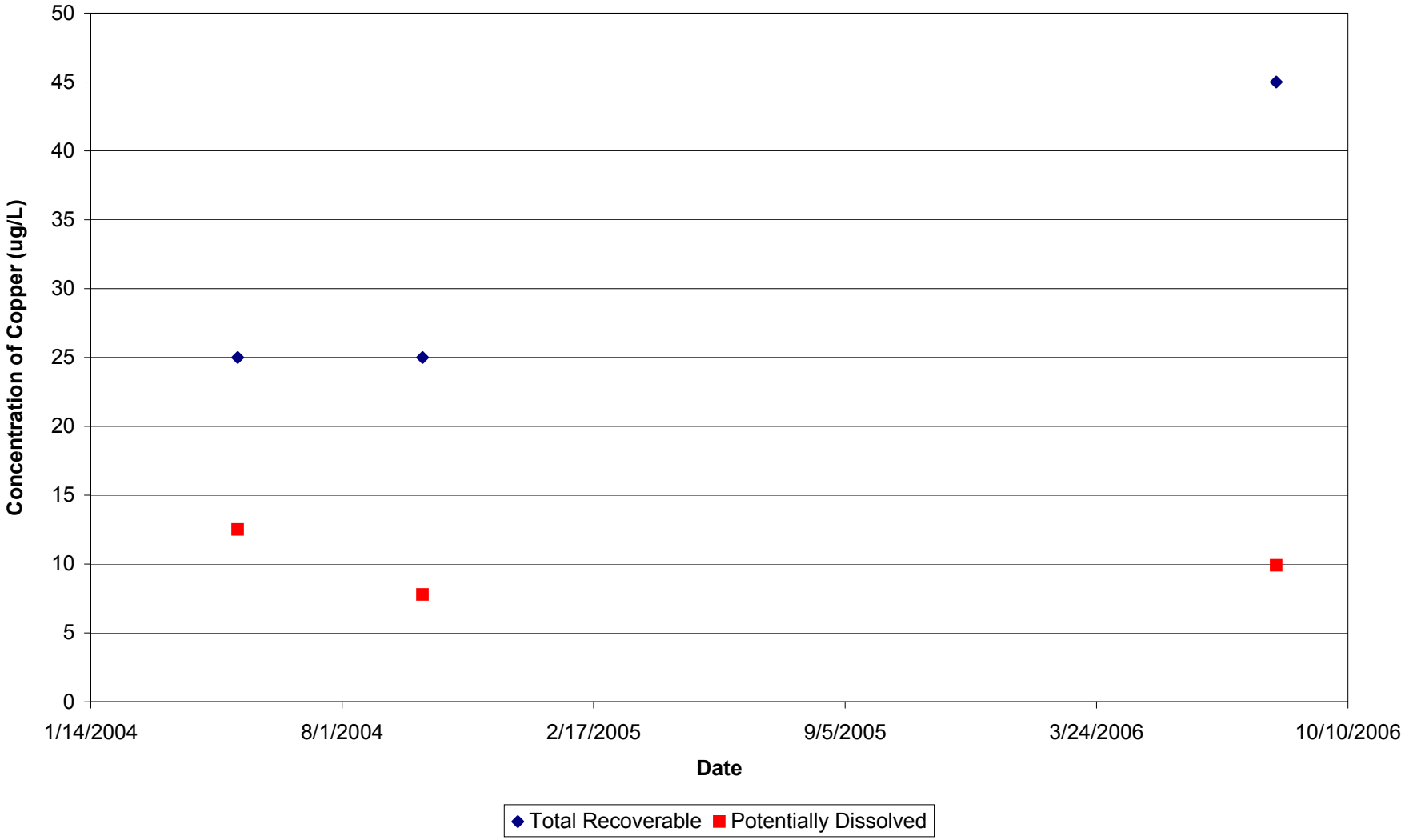
Comparison of Measured Total Recoverable and Potentially Dissolved Copper Concentrations in the Marcy Gulch WWTP Effluent



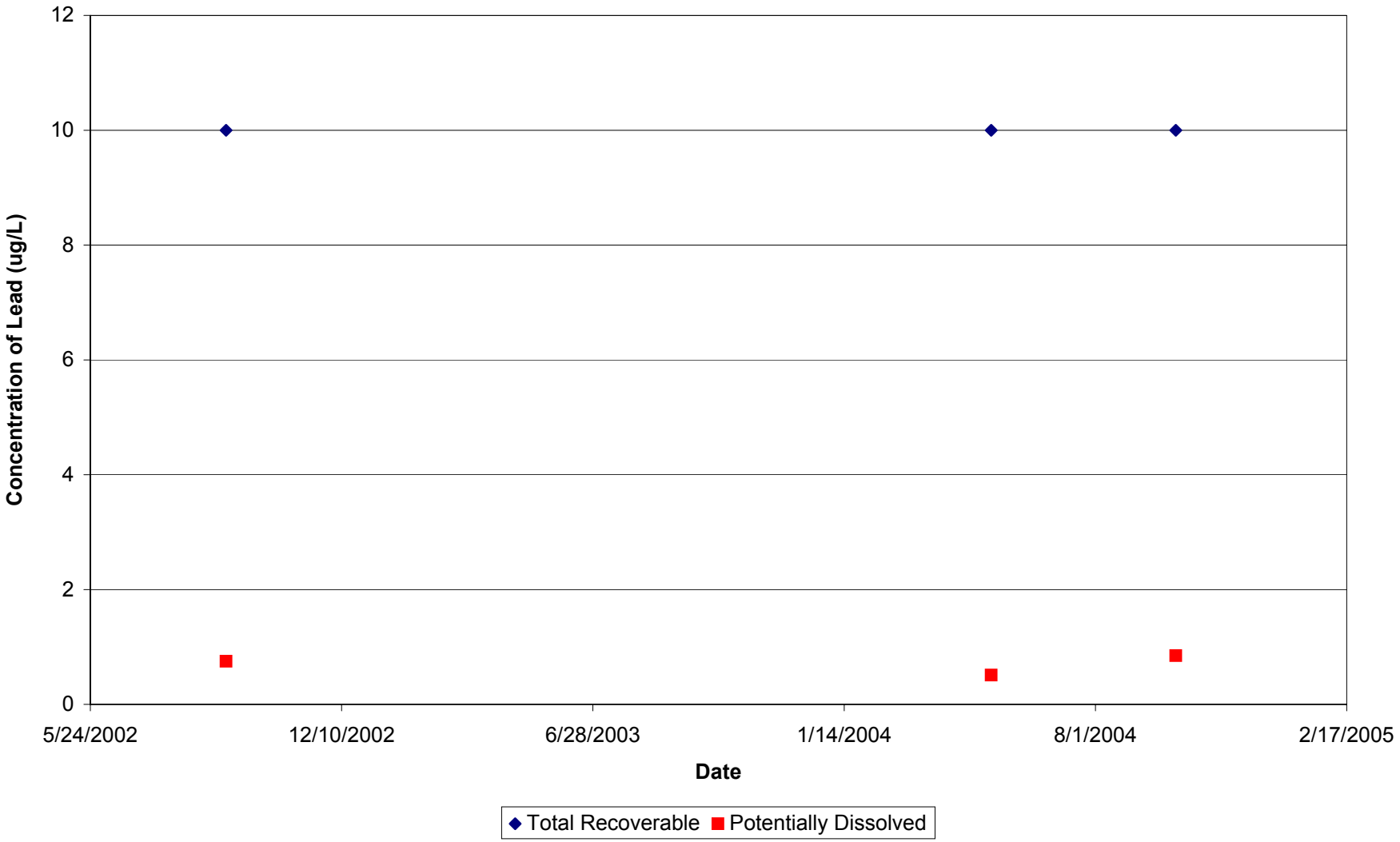
Comparison of Measured Total Recoverable and Potentially Dissolved Cadmium Concentrations in the Littleton Englewood WWTP Effluent



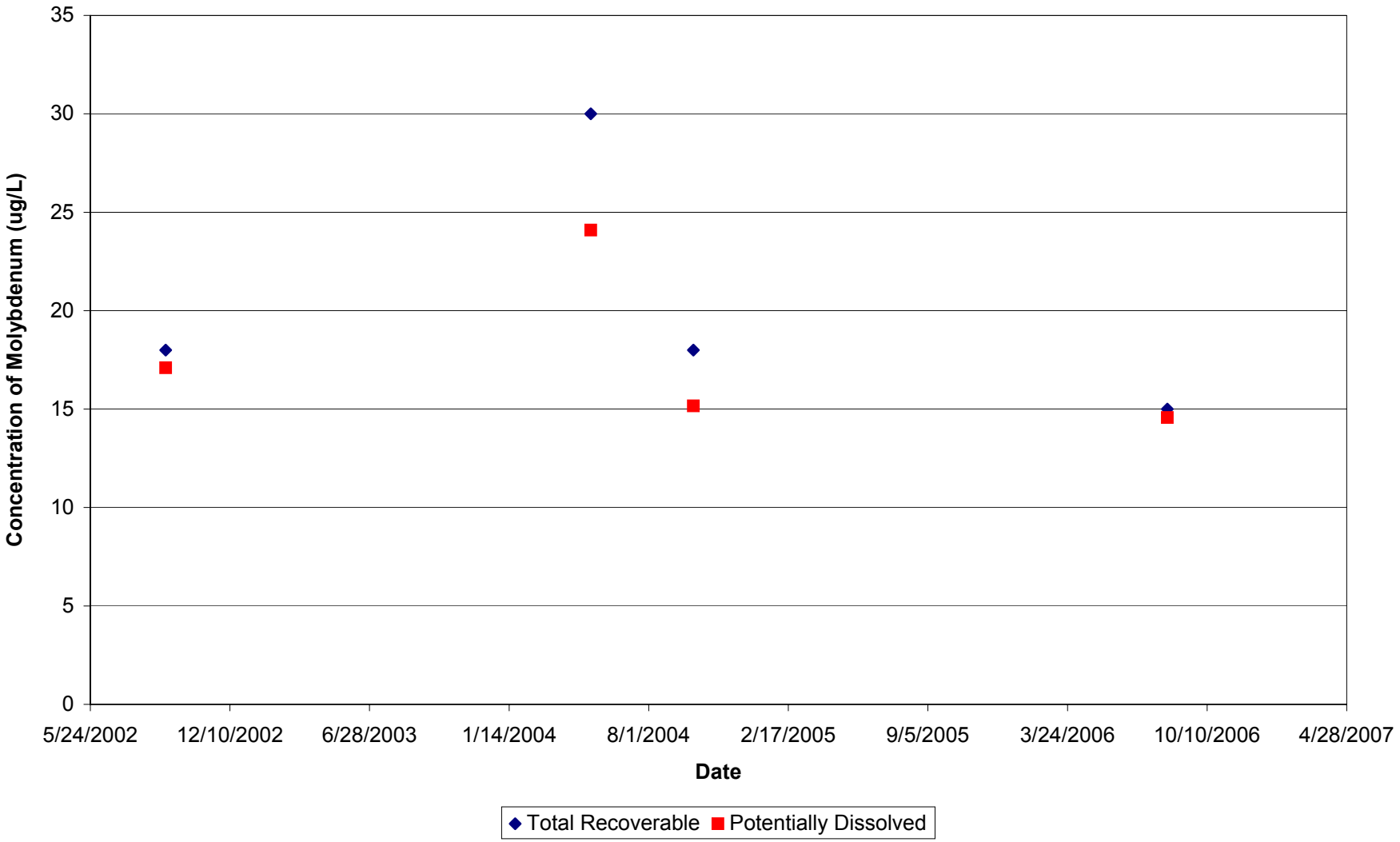
Comparison of Measured Total Recoverable and Potentially Dissolved Copper Concentrations in the Littleton Englewood WWTP Effluent



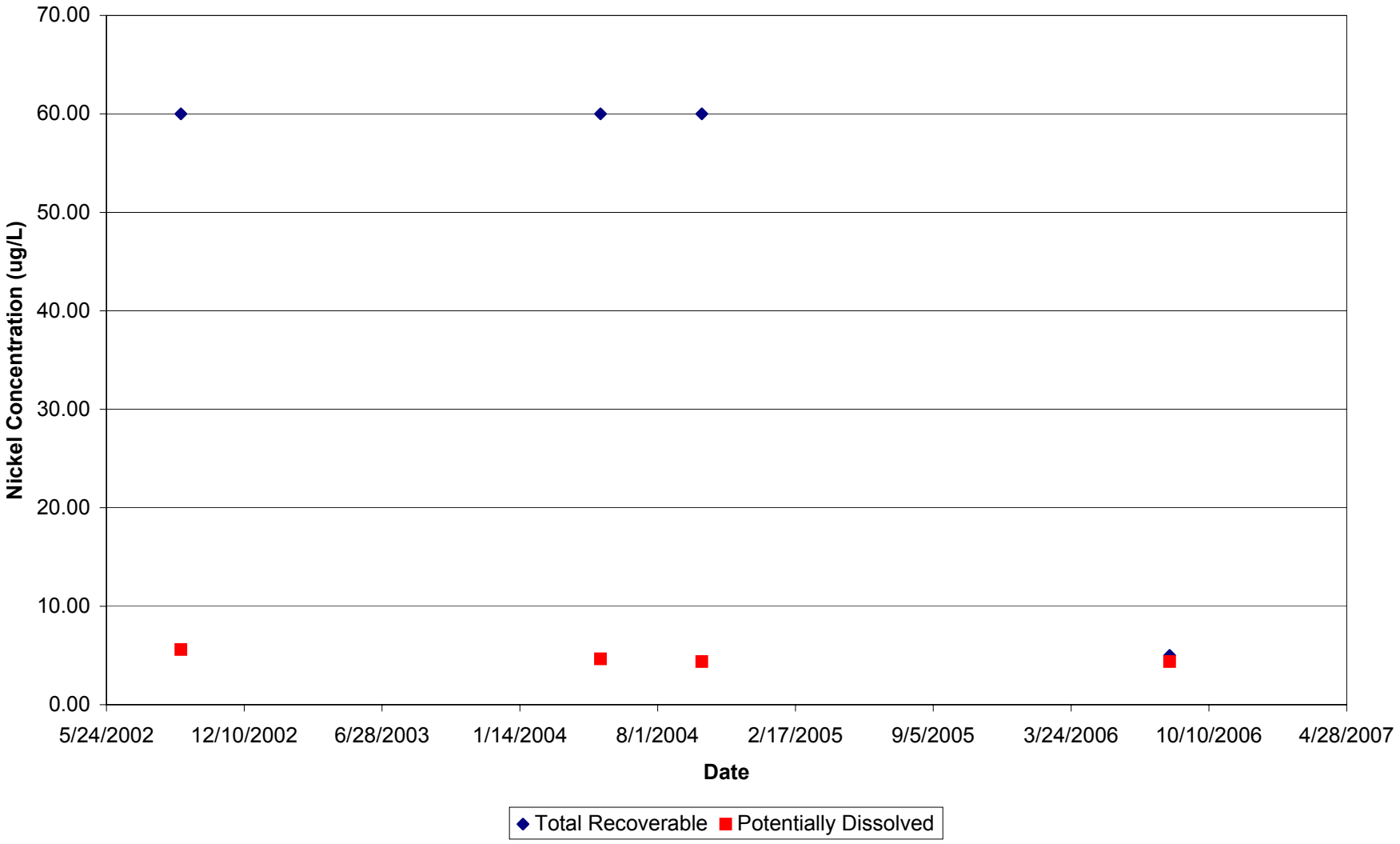
Comparison of Measured Total Recoverable and Potentially Dissolved Lead Concentrations in the Littleton Englewood WWTP Effluent



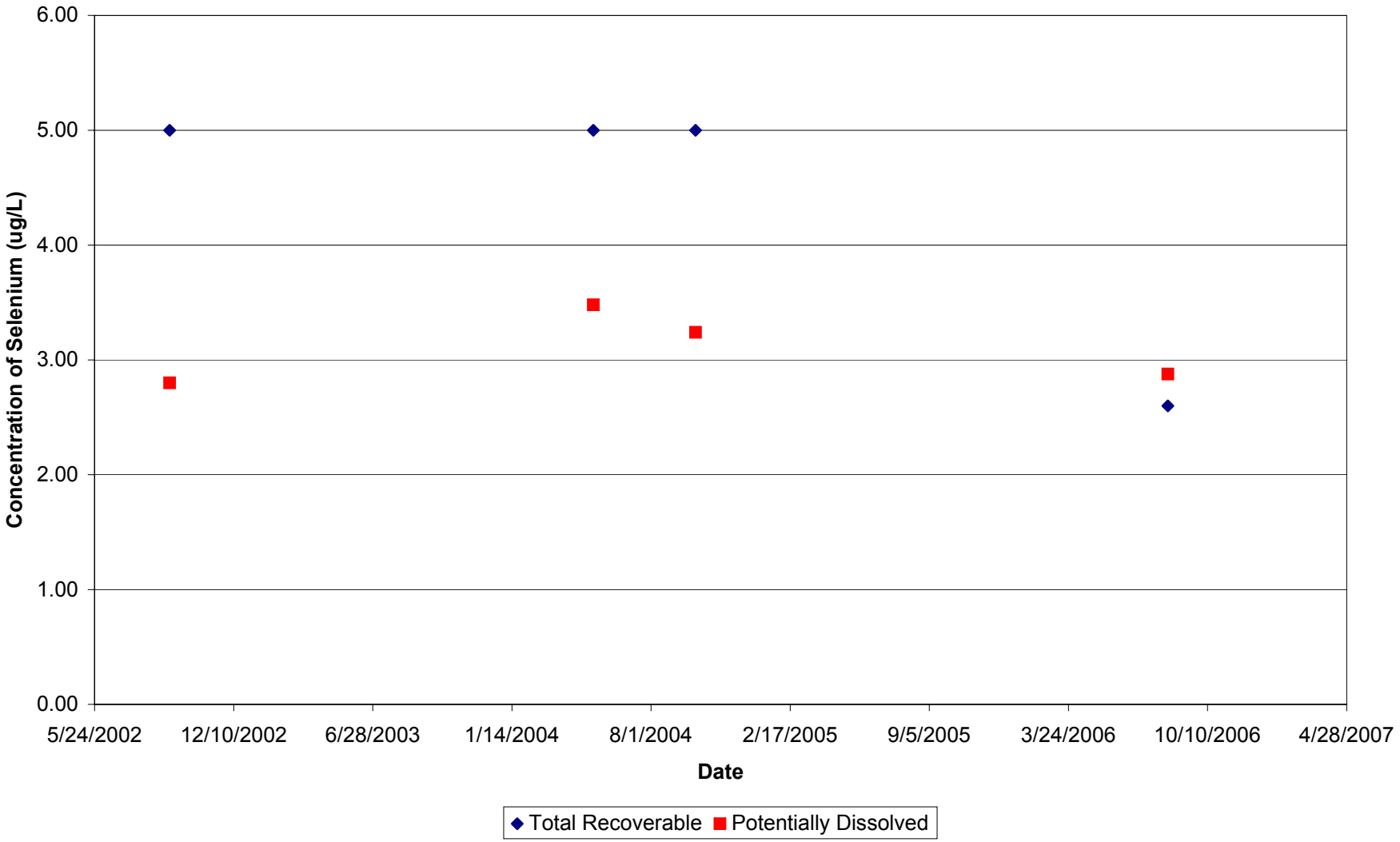
Comparison of Measured Total Recoverable and Potentially Dissolved Molybdenum Concentrations in the Littleton Englewood WWTP Effluent



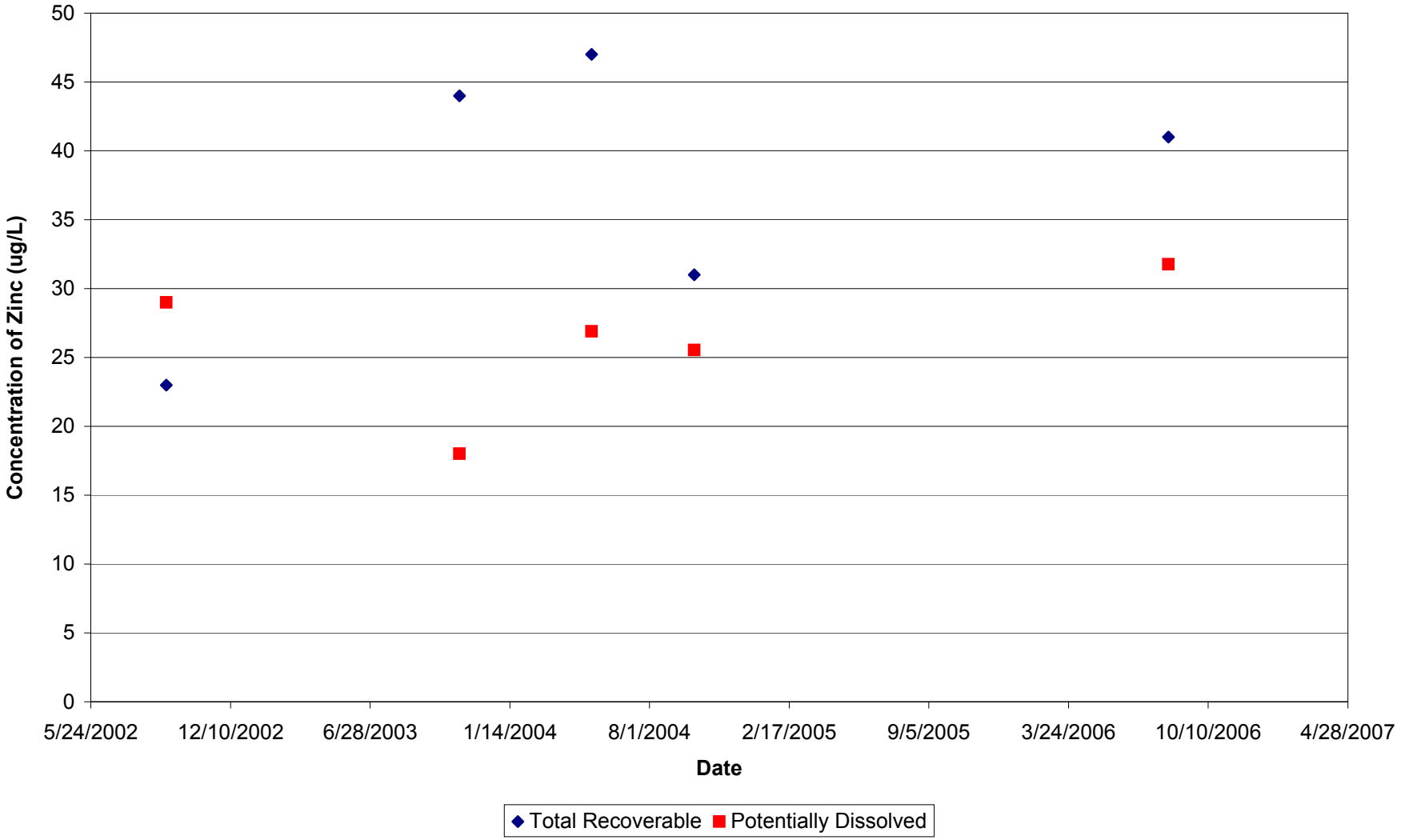
Comparison of Measured Total Recoverable and Potentially Dissolved Nickel Concentrations in the Littleton Englewood WWTP Effluent



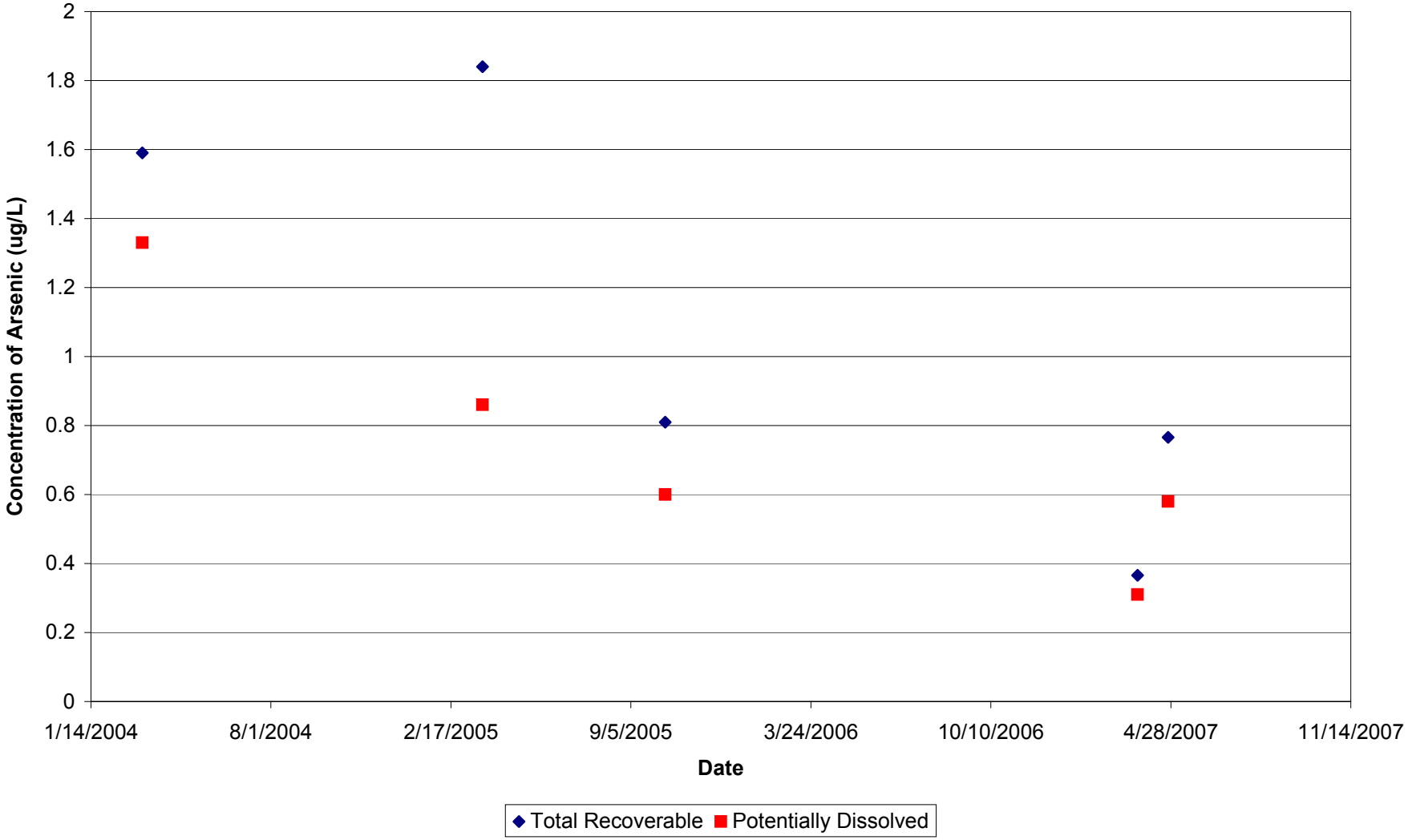
Comparison of Measured Total Recoverable and Potentially Dissolved Selenium Concentrations in the Littleton Englewood WWTP Effluent



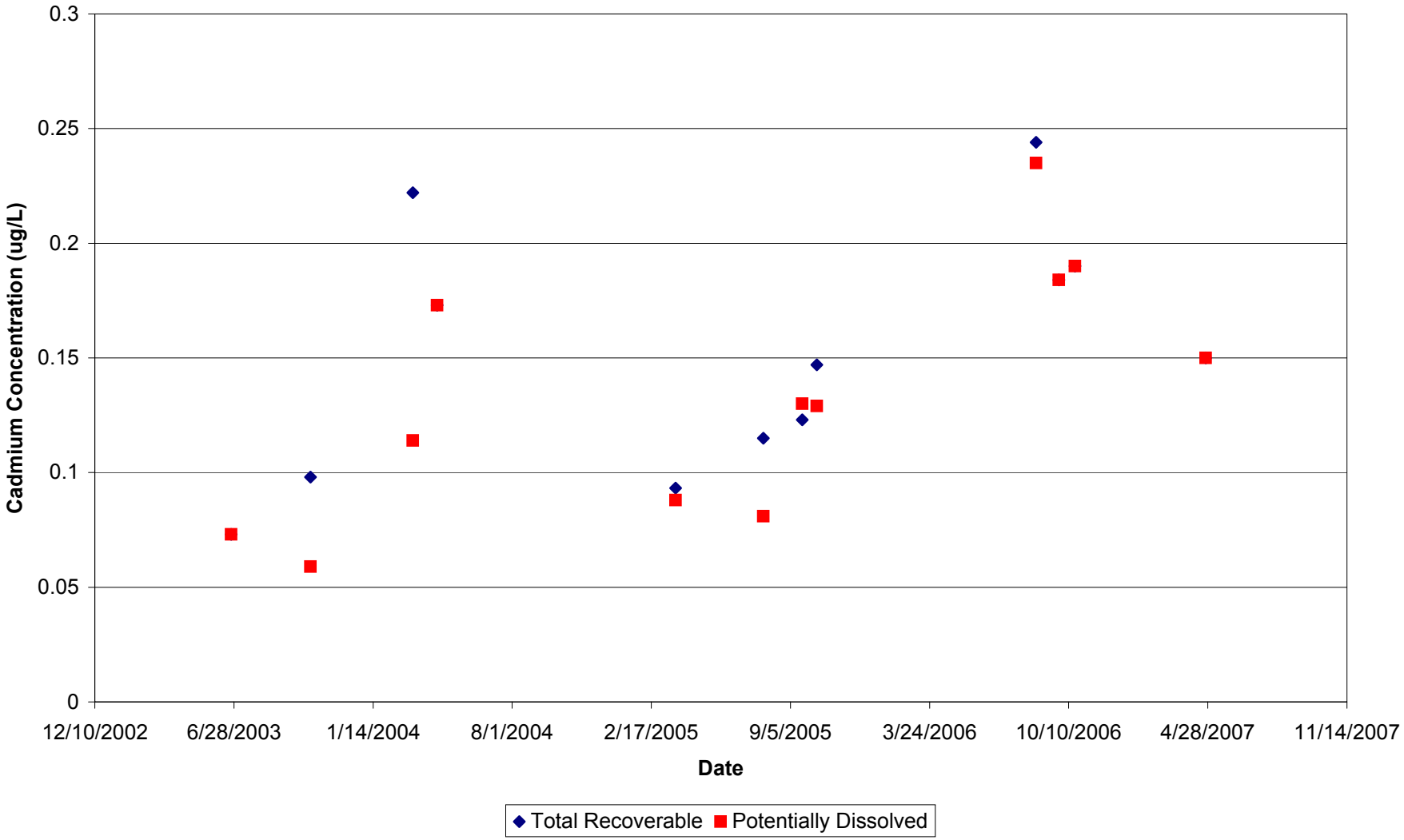
Comparison of Measured Total Recoverable and Potentially Dissolved Zinc Concentrations in the Littleton Englewood WWTP Effluent



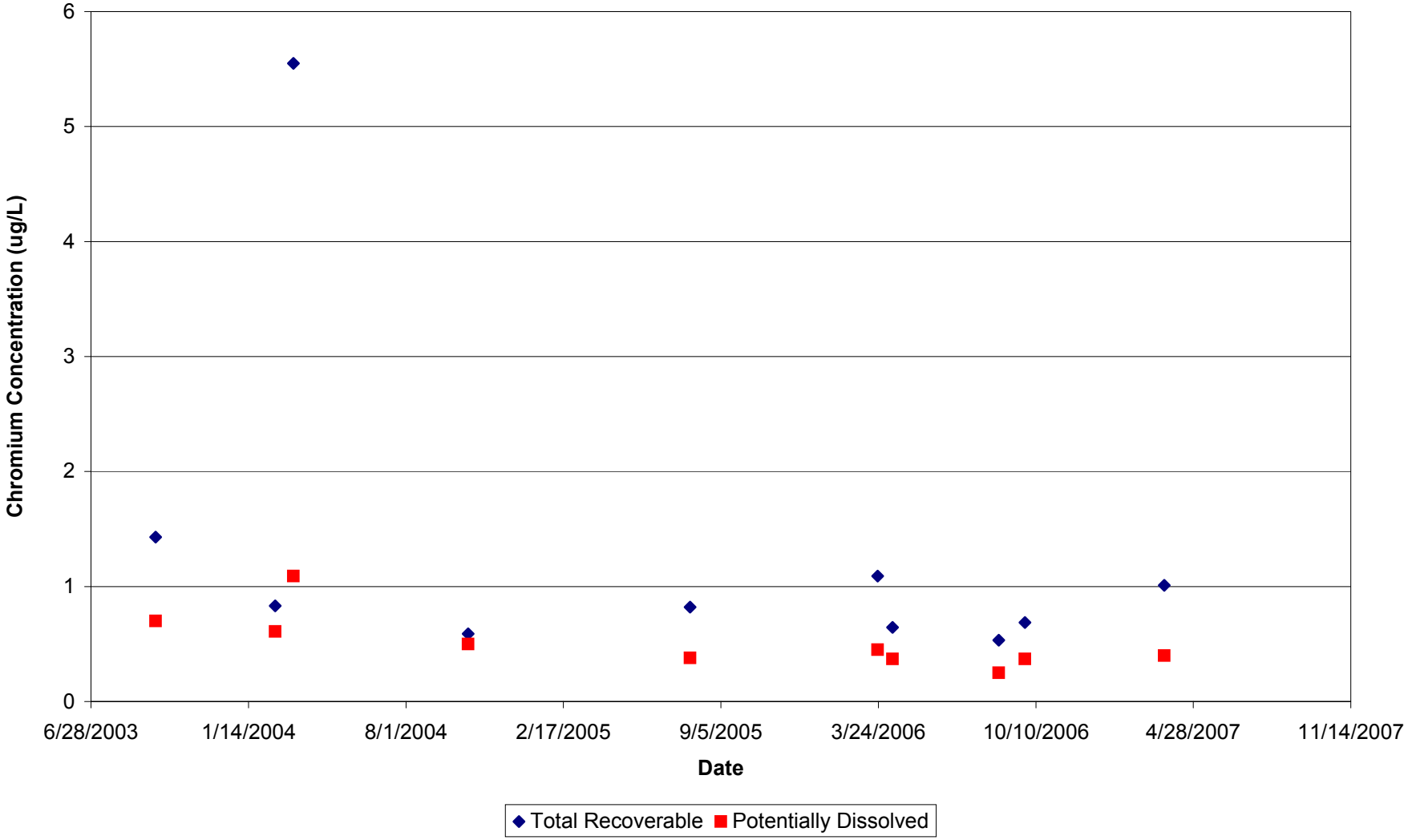
Comparison of Measured Total Recoverable and Potentially Dissolved Arsenic Concentrations in the City of Pueblo WWTP Effluent



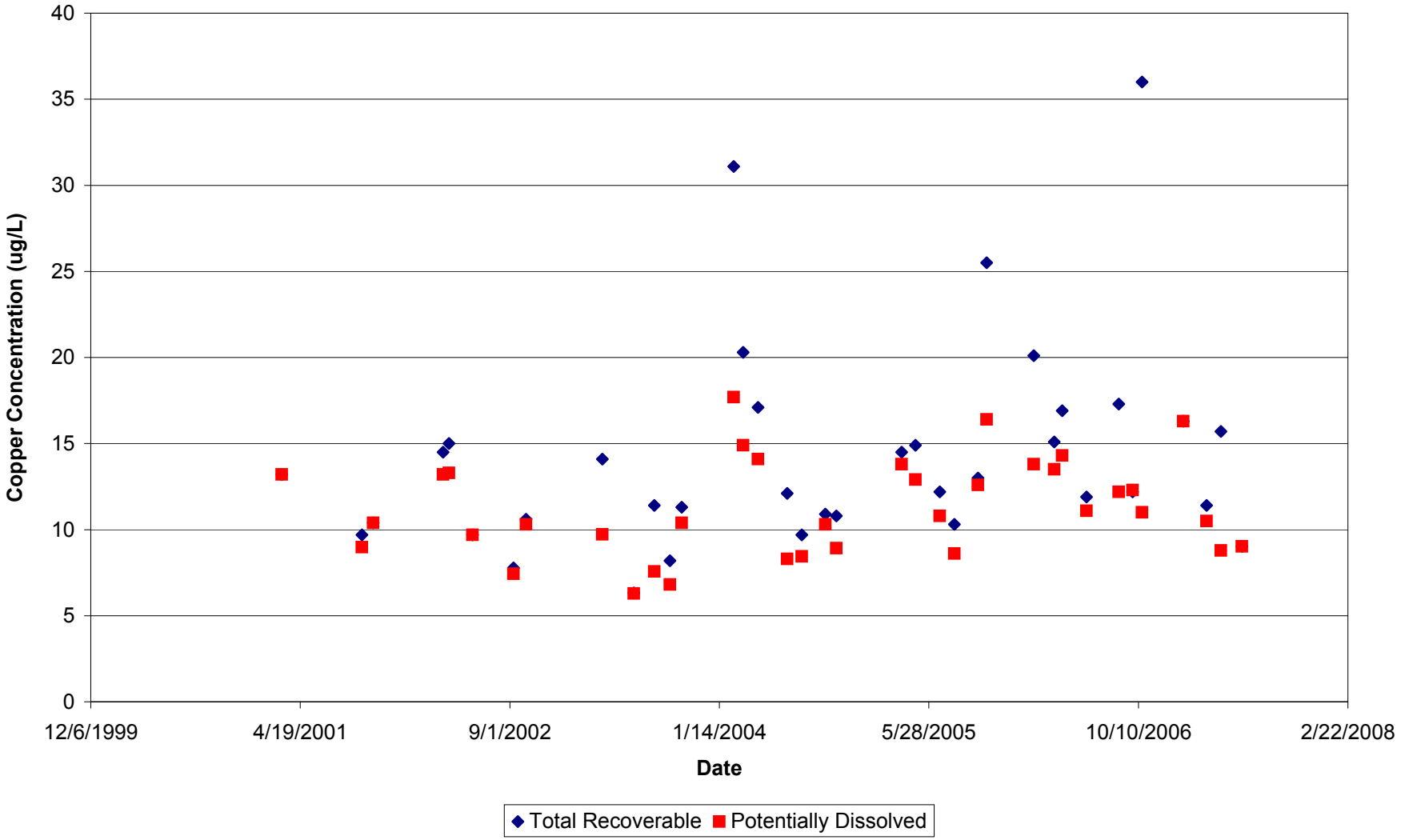
Comparison of Measured Total Recoverable and Potentially Dissolved Cadmium Concentrations in the City of Pueblo WWTP Effluent



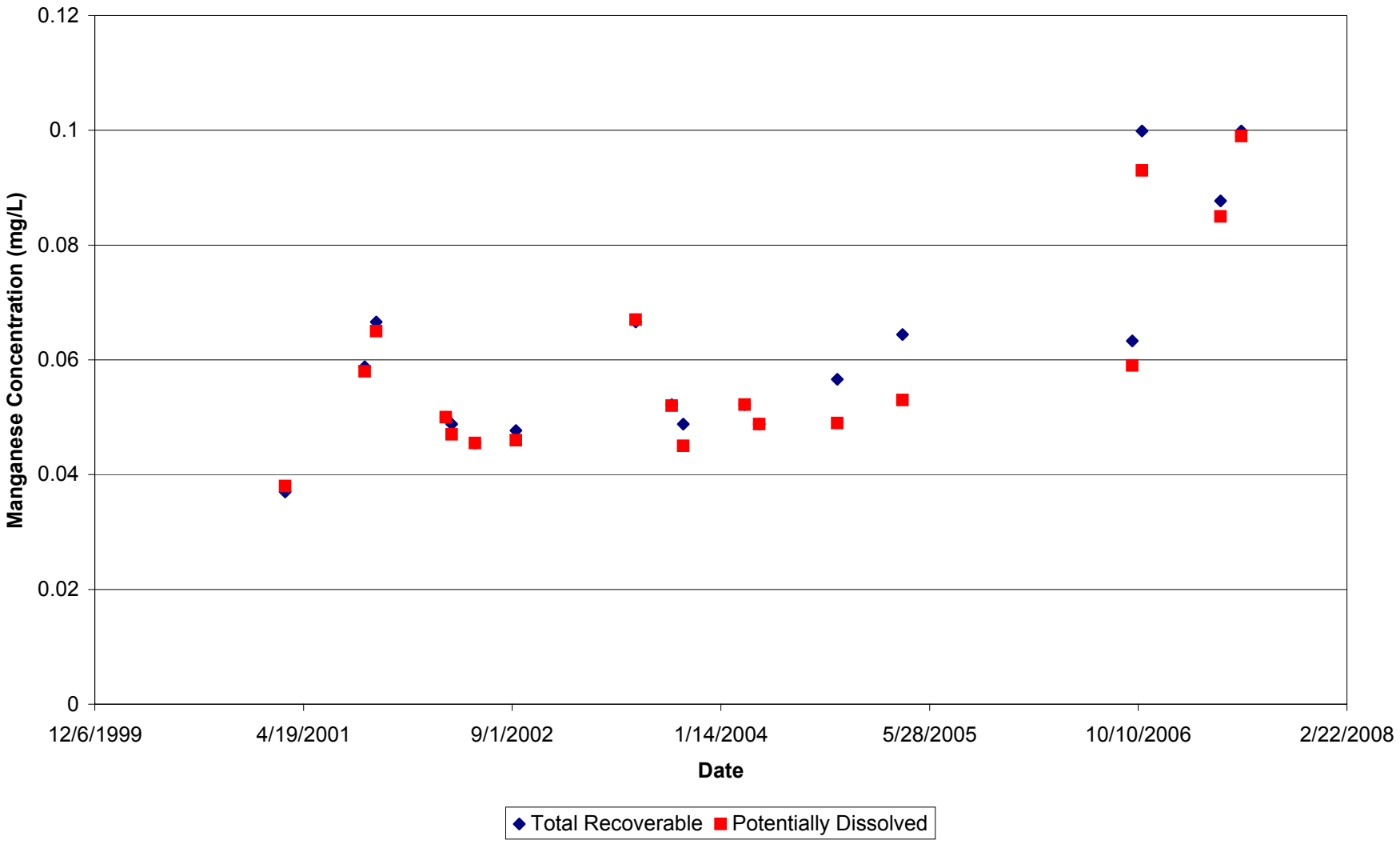
Comparison of Measured Total Recoverable and Potentially Dissolved Chromium Concentrations in the City of Pueblo WWTP Effluent



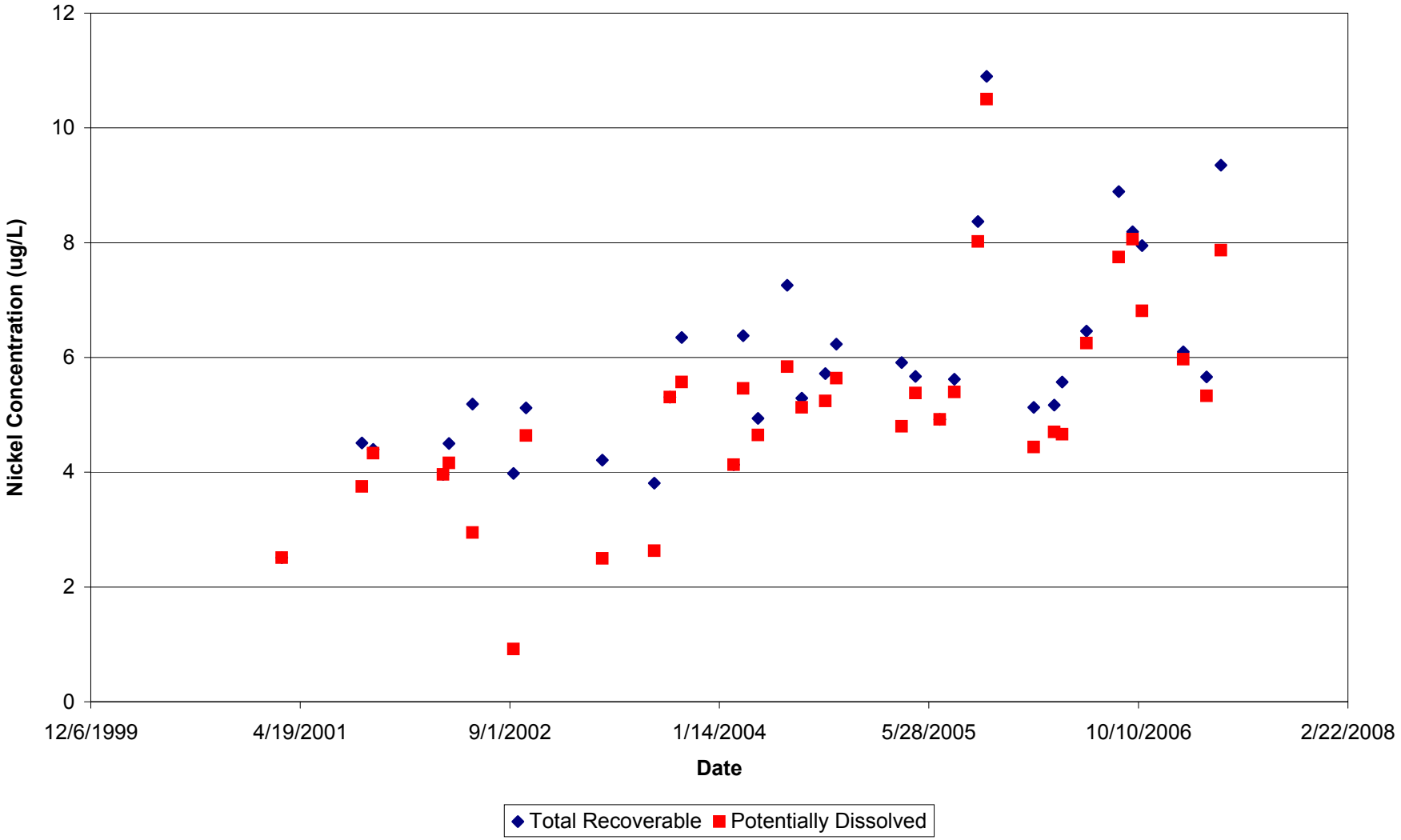
Comparison of Measured Total Recoverable and Potentially Dissolved Copper Concentrations in the City of Pueblo WWTP Effluent



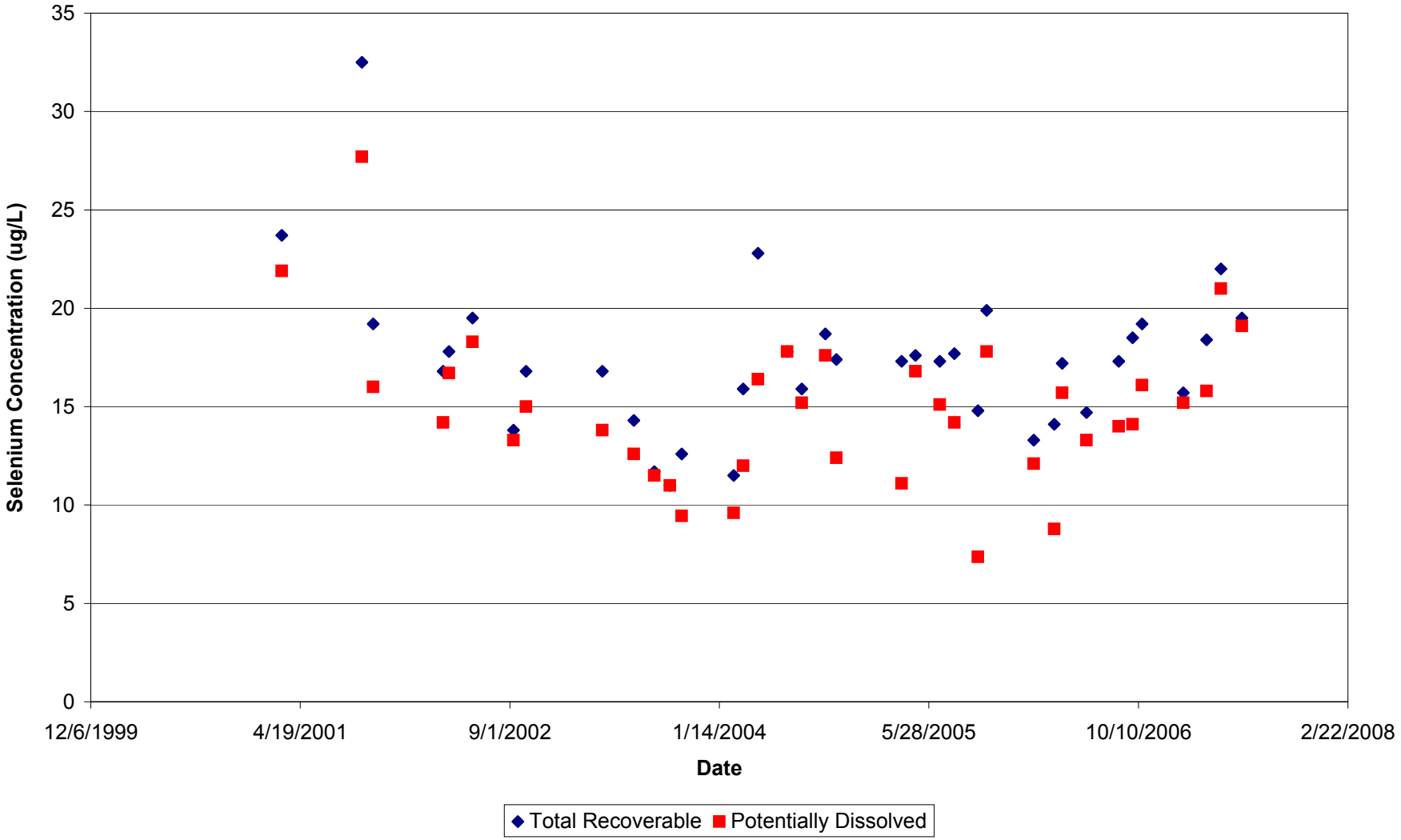
Comparison of Measured Total Recoverable and Potentially Dissolved Manganese Concentrations in the City of Pueblo WWTP Effluent



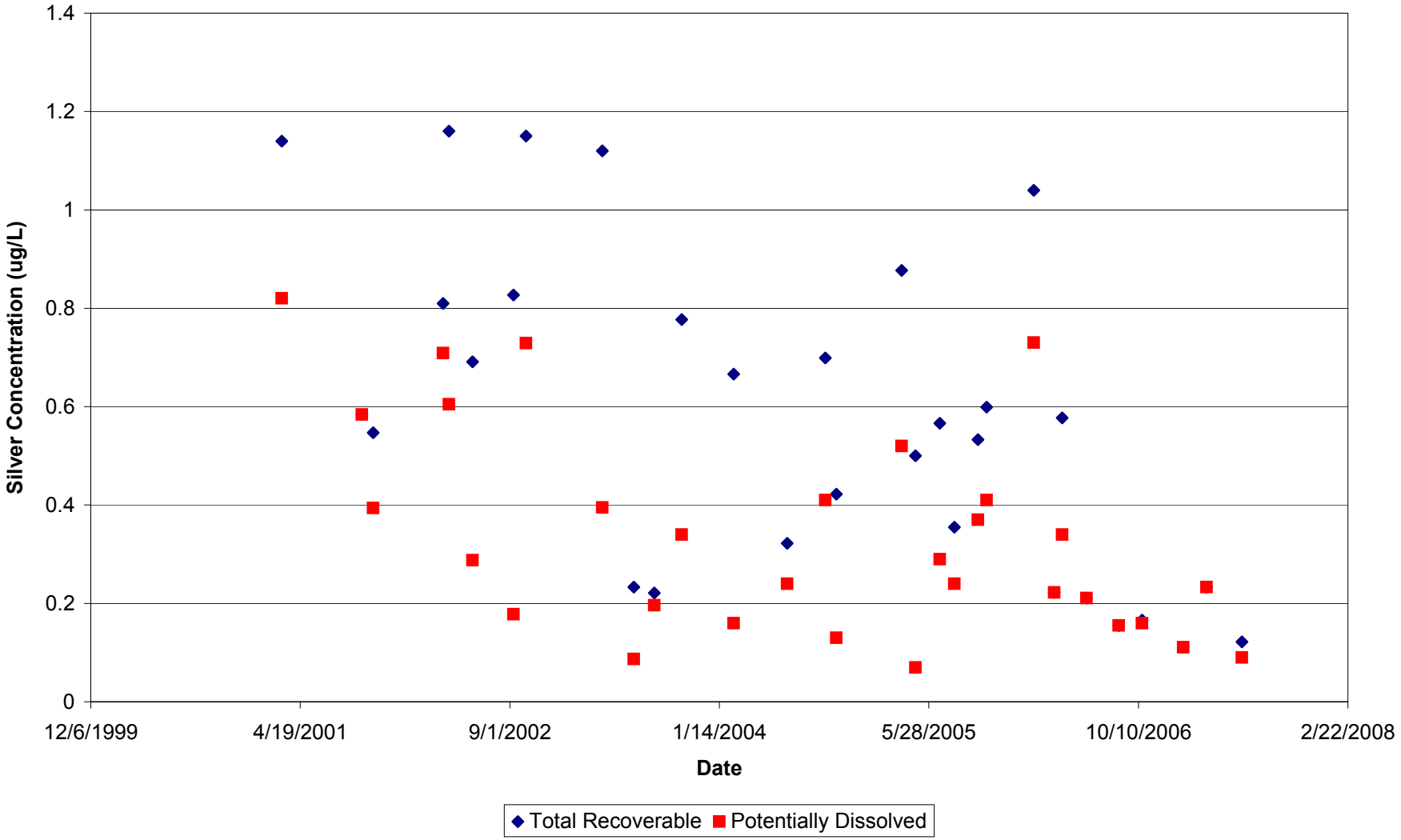
Comparison of Measured Total Recoverable and Potentially Dissolved Nickel Concentrations in the City of Pueblo WWTP Effluent



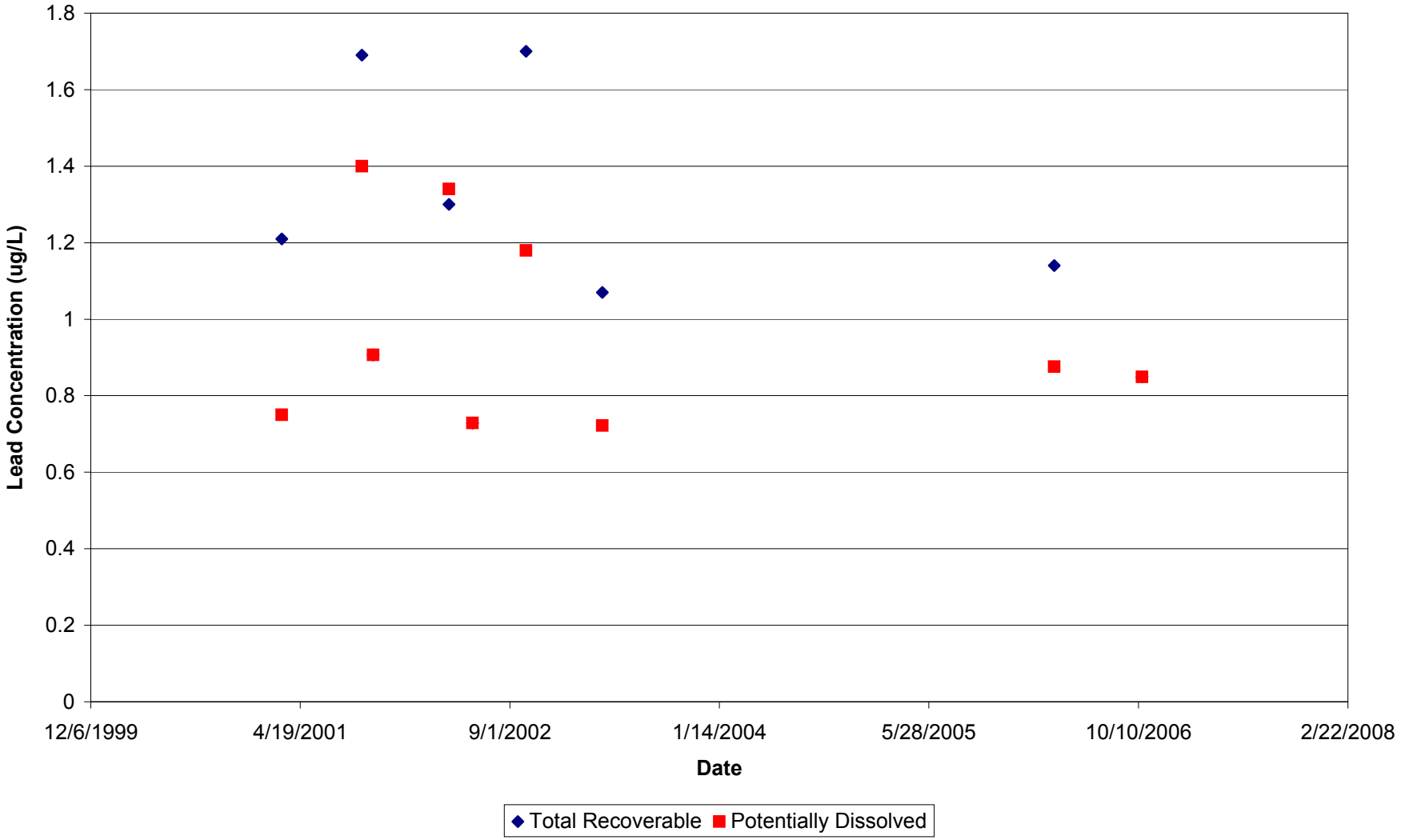
Comparison of Measured Total Recoverable and Potentially Dissolved Selenium Concentrations in the City of Pueblo WWTP Effluent



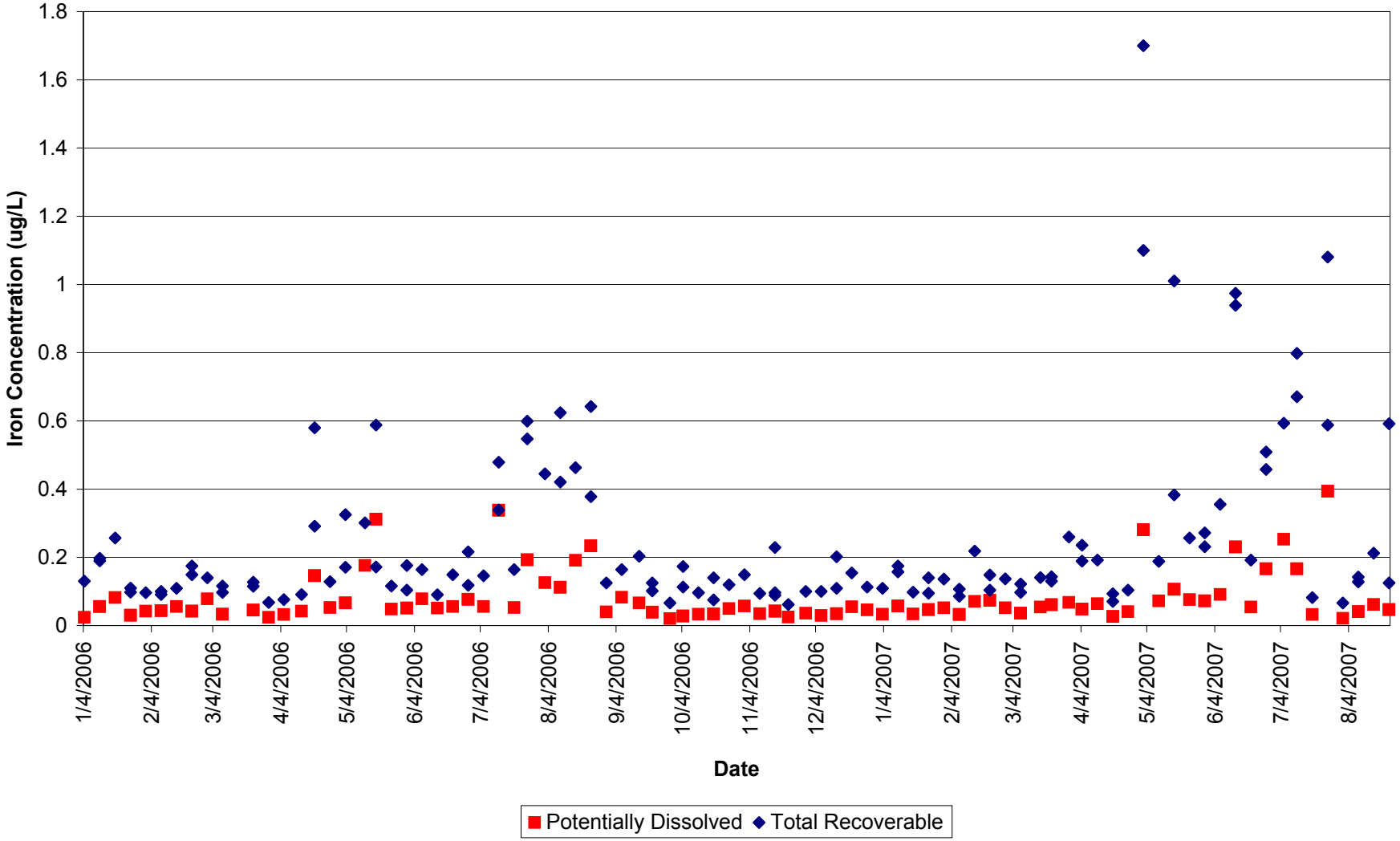
Comparison of Measured Total Recoverable and Potentially Dissolved Silver Concentrations in the City of Pueblo WWTP Effluent



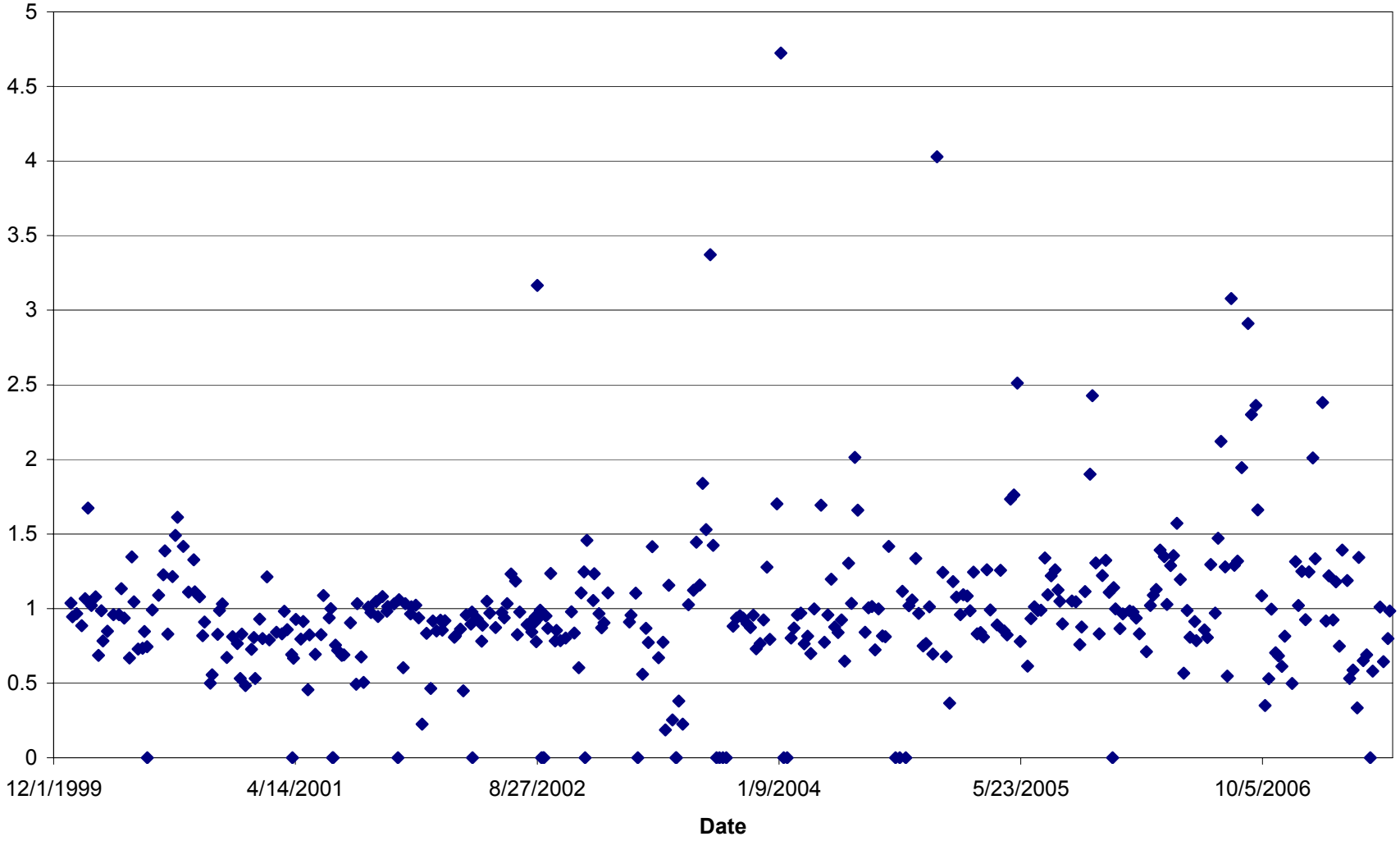
Comparison of Measured Total Recoverable and Potentially Dissolved Lead Concentrations in the City of Pueblo WWTP Effluent



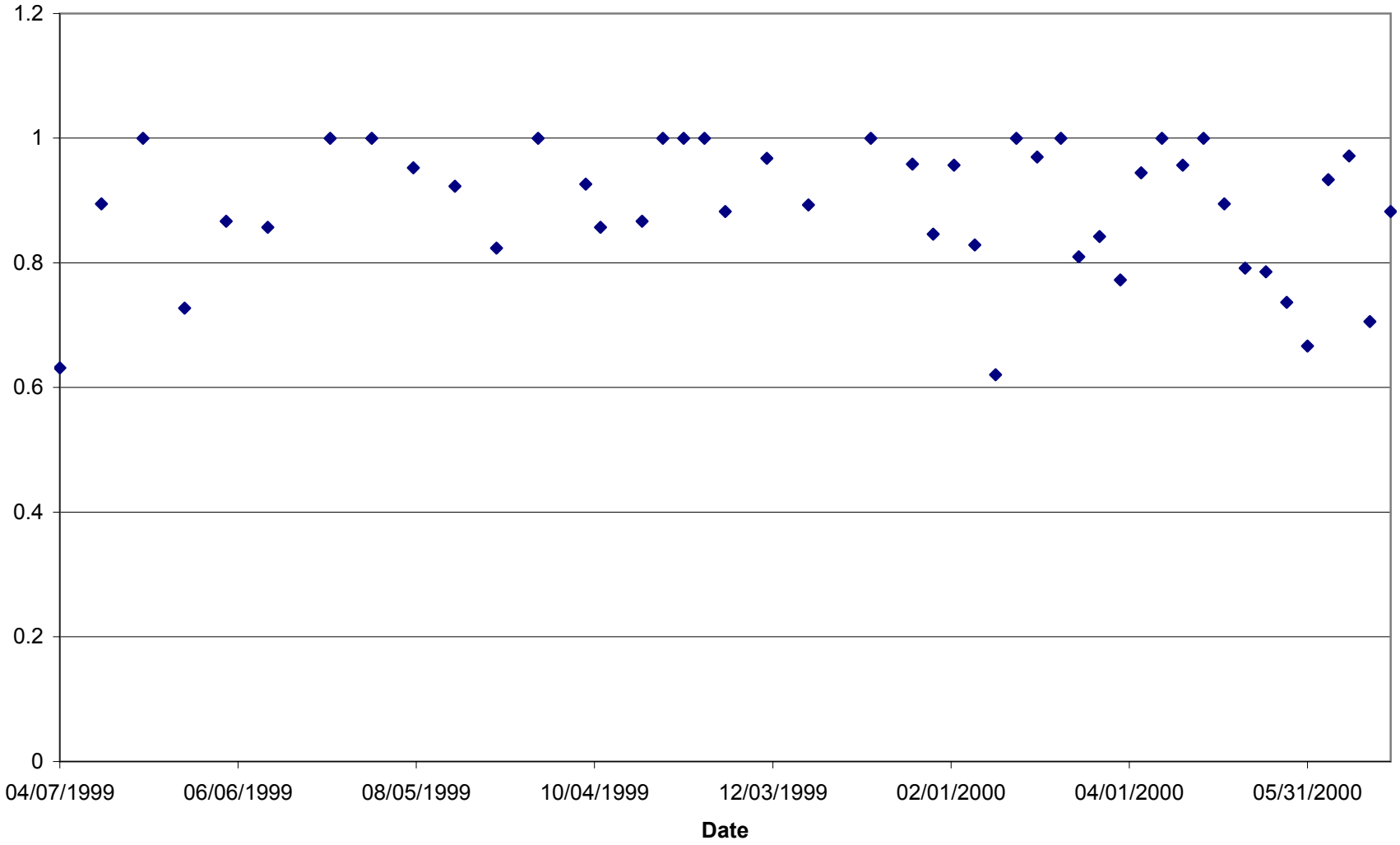
Comparison of Measured Total Recoverable and Potentially Dissolved Iron Concentrations in Xcel's Effluent (Leggett 001)



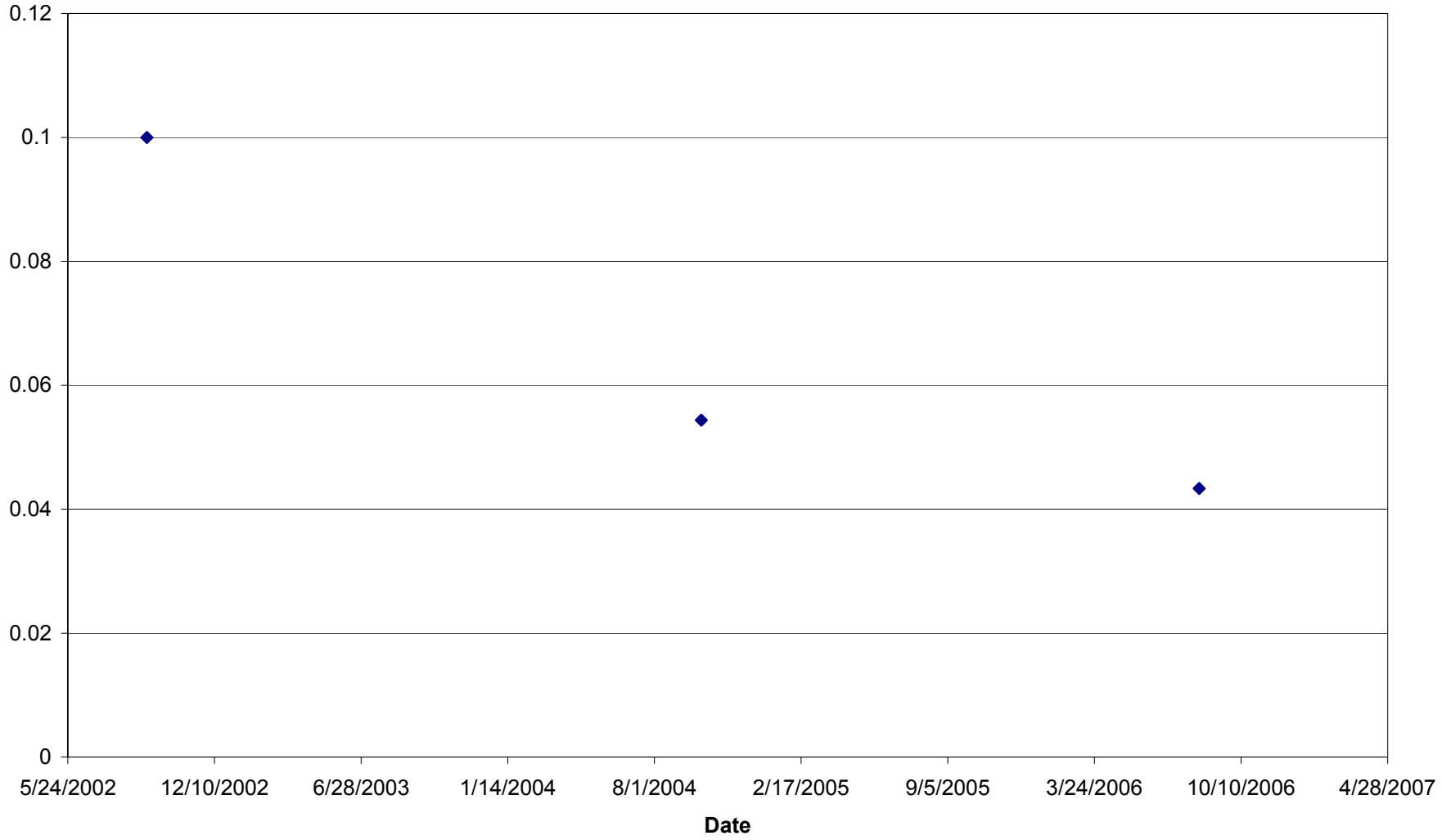
Ratio of Measured Potentially Dissolved and Total Recoverable Copper Concentrations in the City of Boulder WWTP Effluent



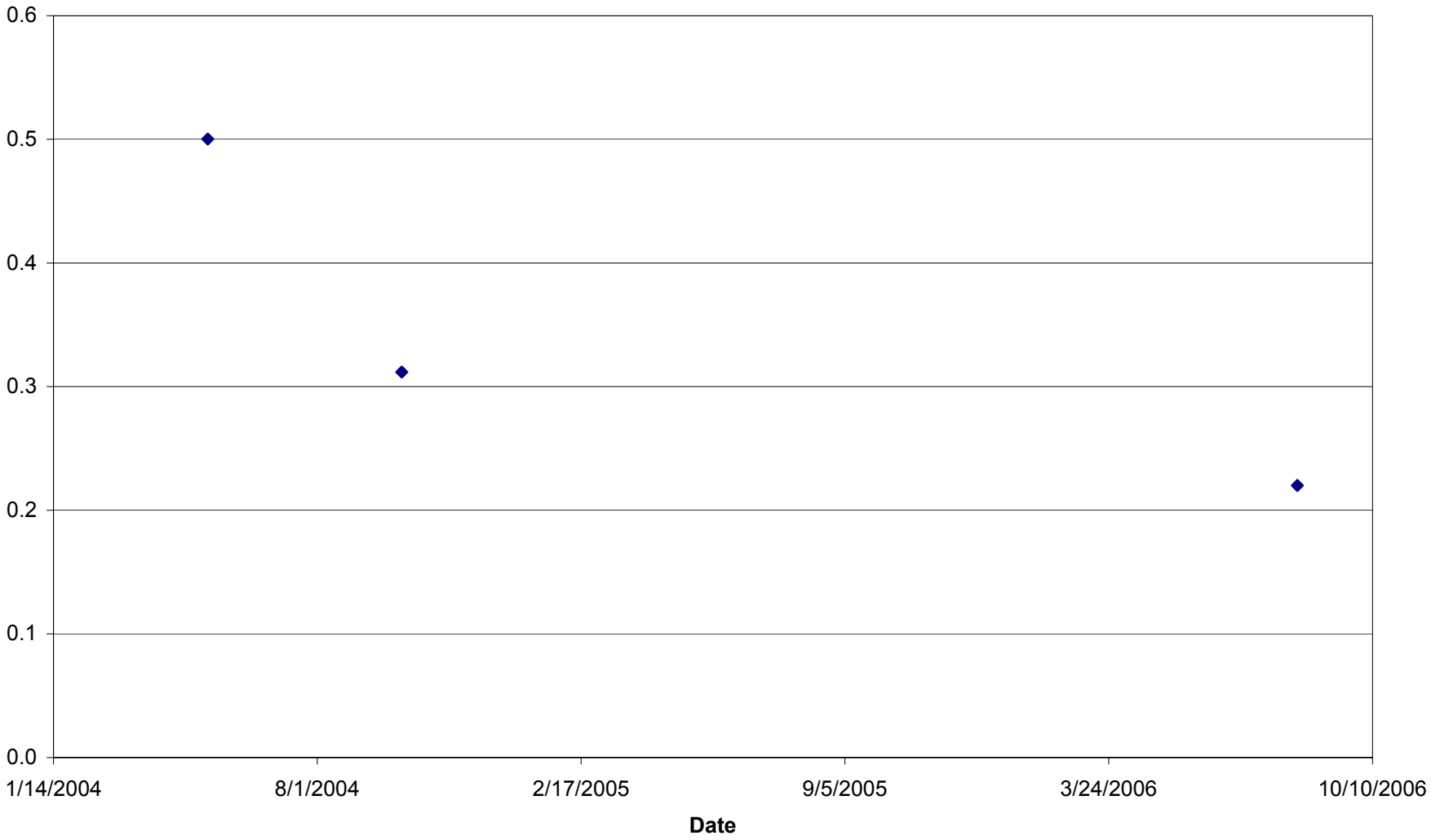
Ratio of Measured Potentially Dissolved and Total Recoverable Copper Concentrations in the Marcy Gulch WWTP Effluent



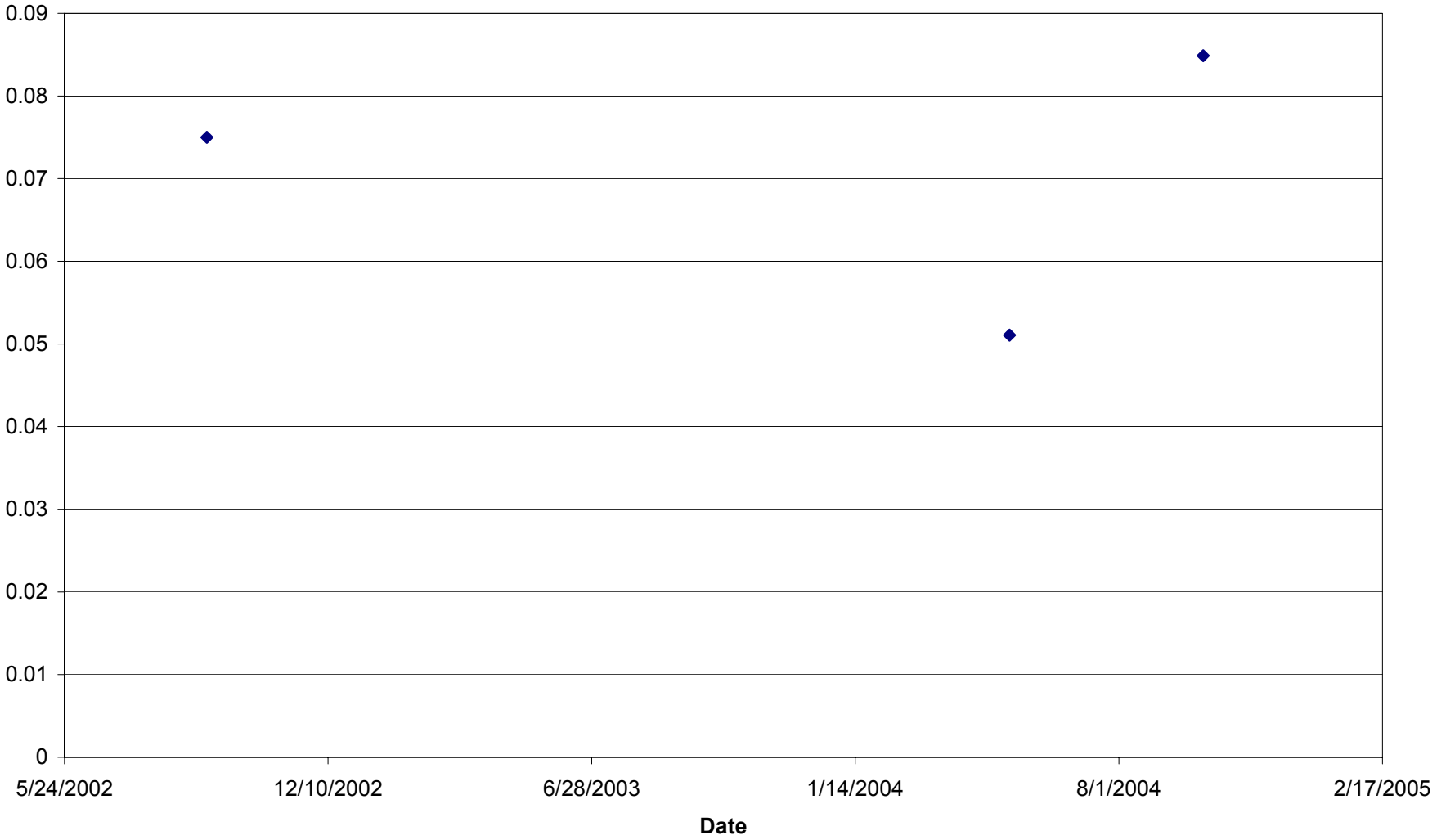
Ratio of Measured Potentially Dissolved and Total Recoverable Cadmium Concentrations in the Littleton Englewood WWTP Effluent



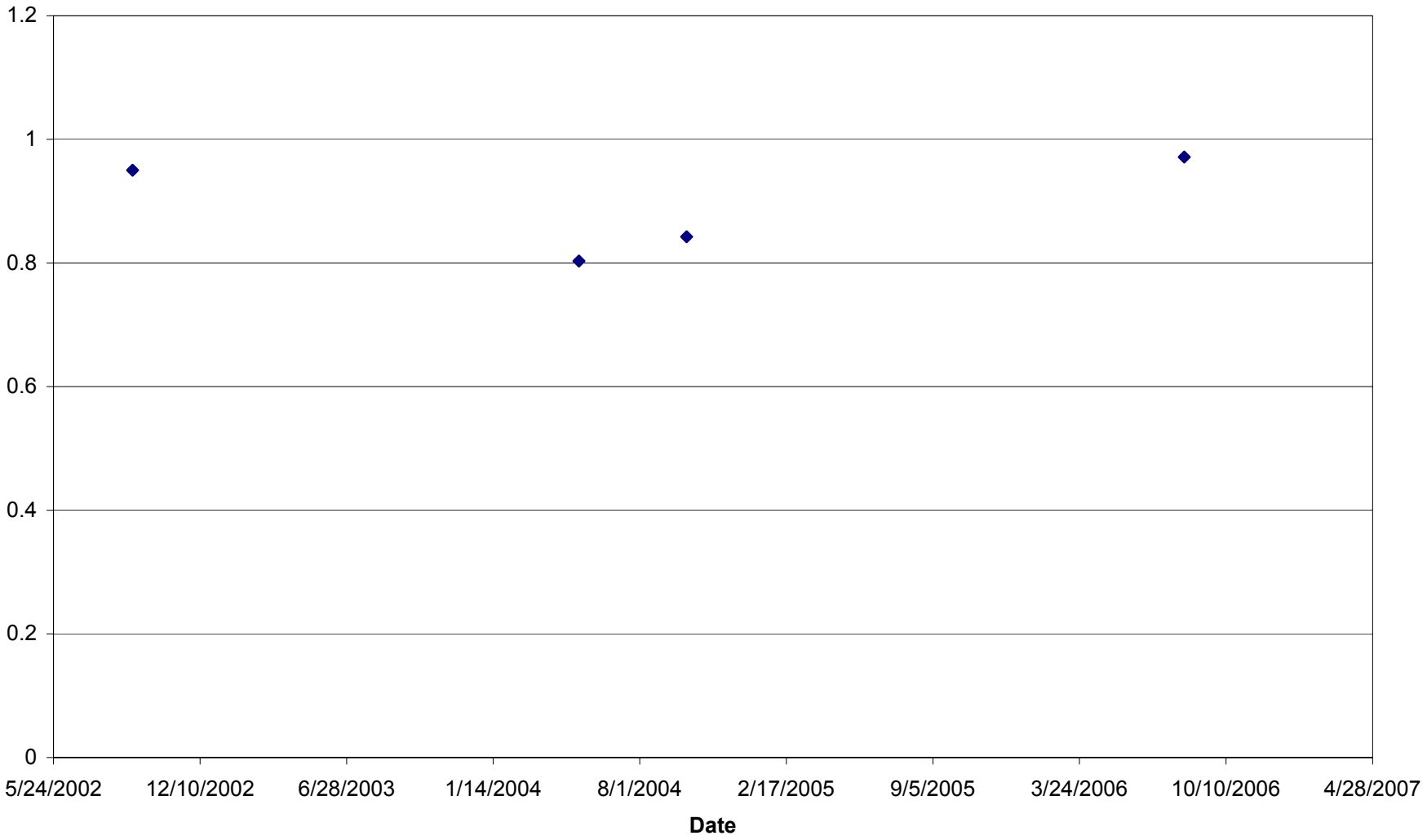
Ratio of Measured Potentially Dissolved and Total Recoverable Copper Concentrations in the Littleton Englewood WWTP Effluent



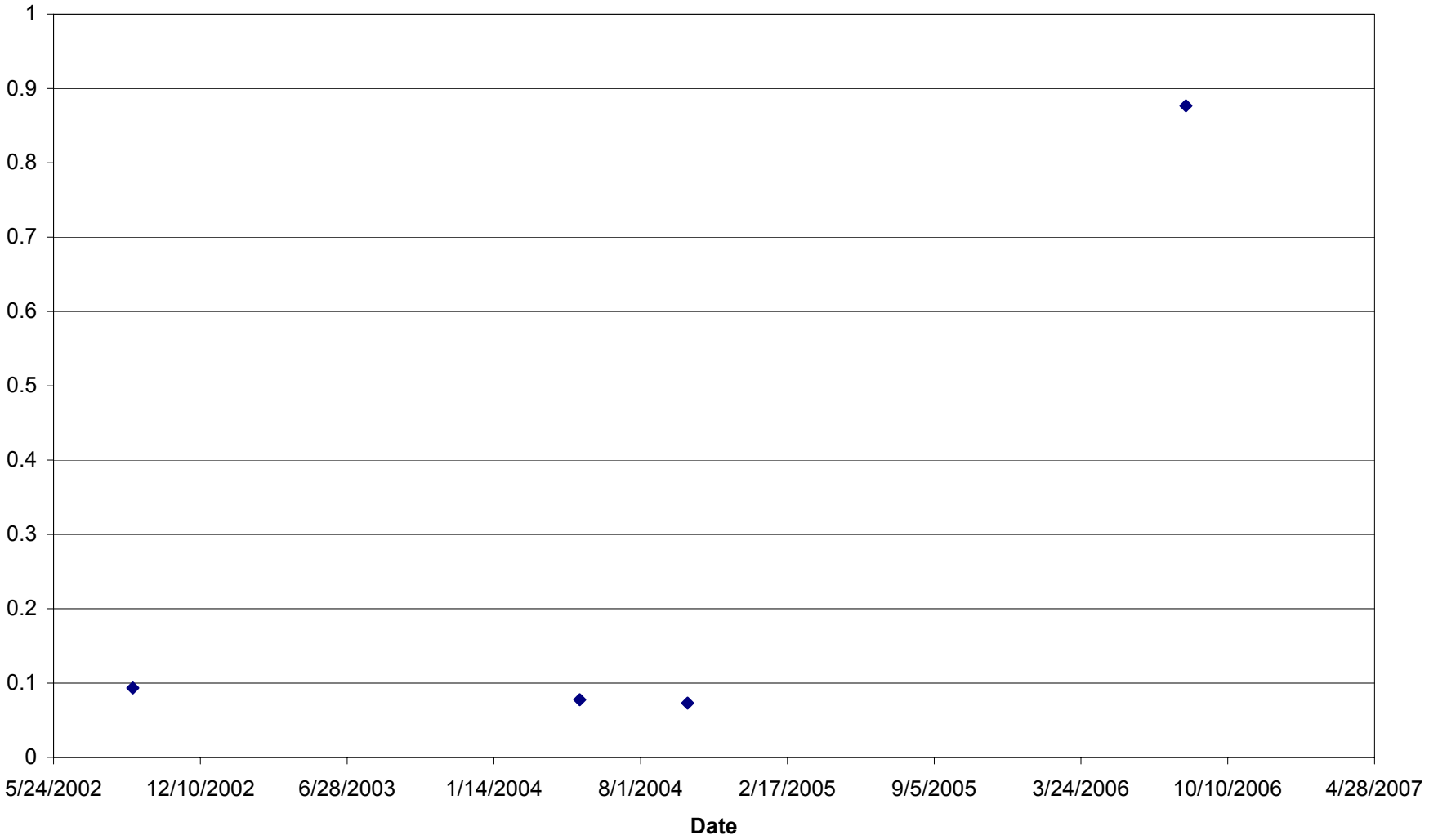
Ratio of Measured Potentially Dissolved and Total Recoverable Lead Concentration in the Littleton Englewood WWTP Effluent



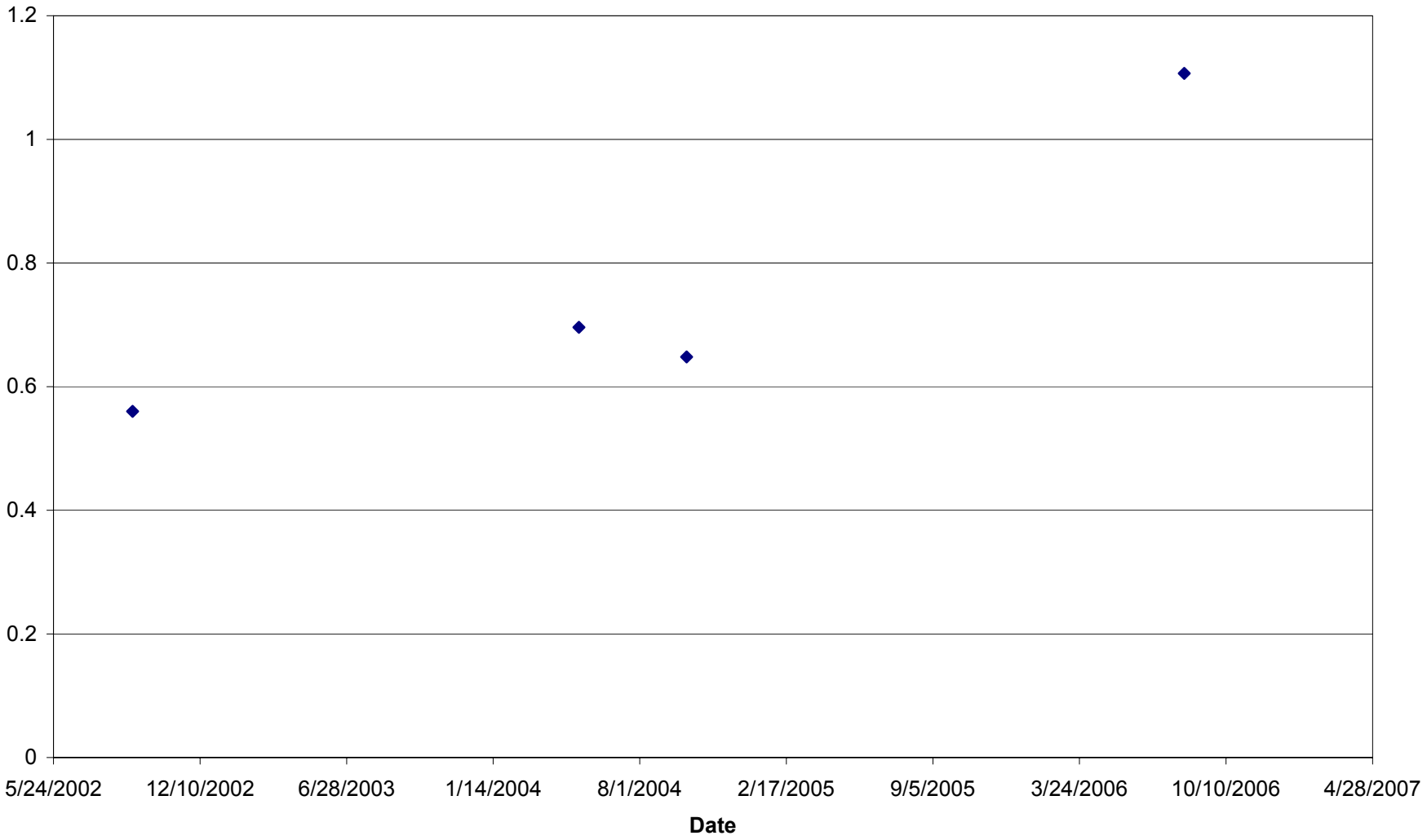
Ratio of Measured Potentially Dissolved and Total Recoverable Molybdenum Concentrations in the Littleton Engleood WWTP Effluent



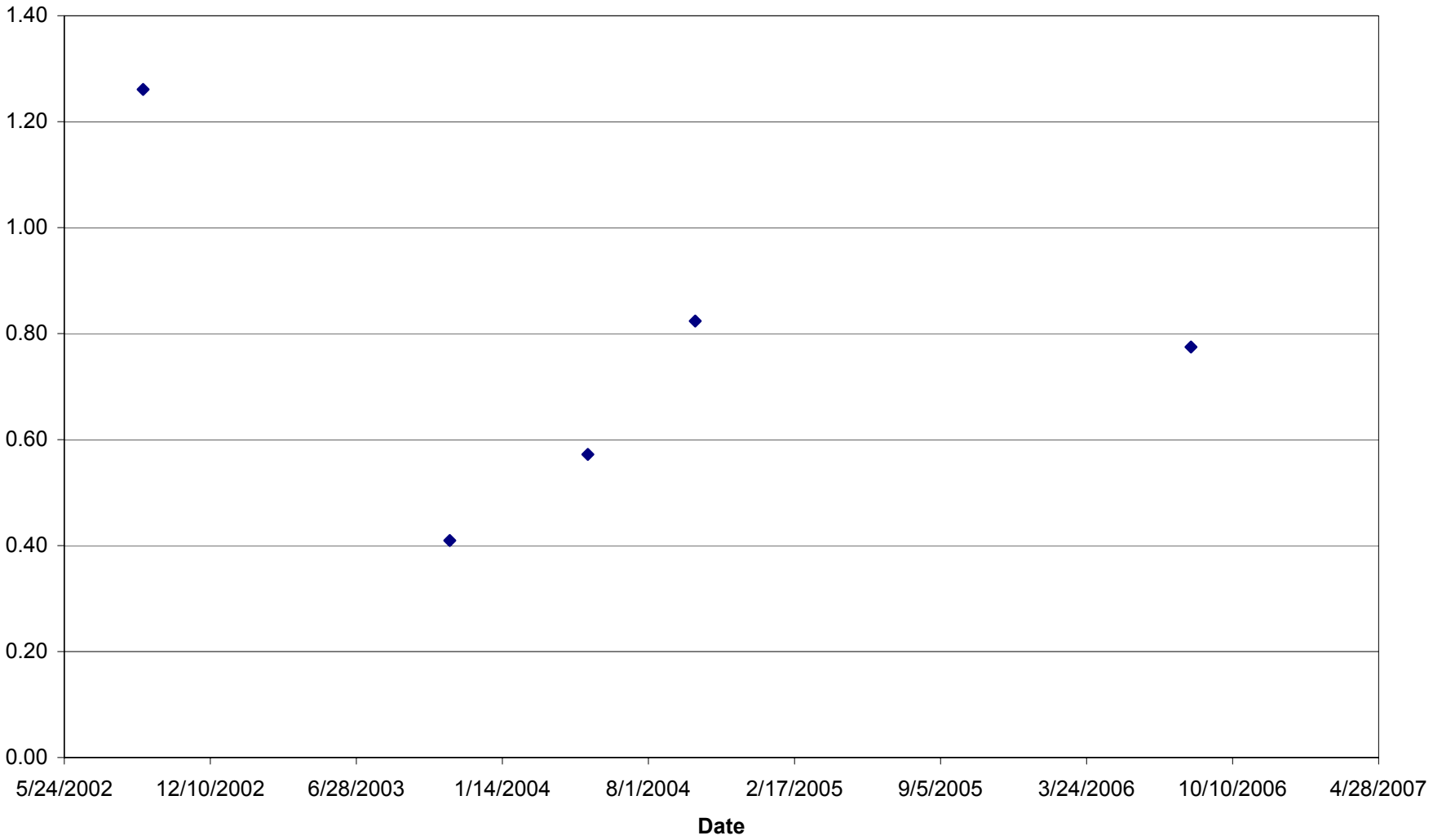
Ratio of Measured Potentially Dissolved and Total Recoverable Nickel Concentrations in the Littleton Englewood WWTP Effluent



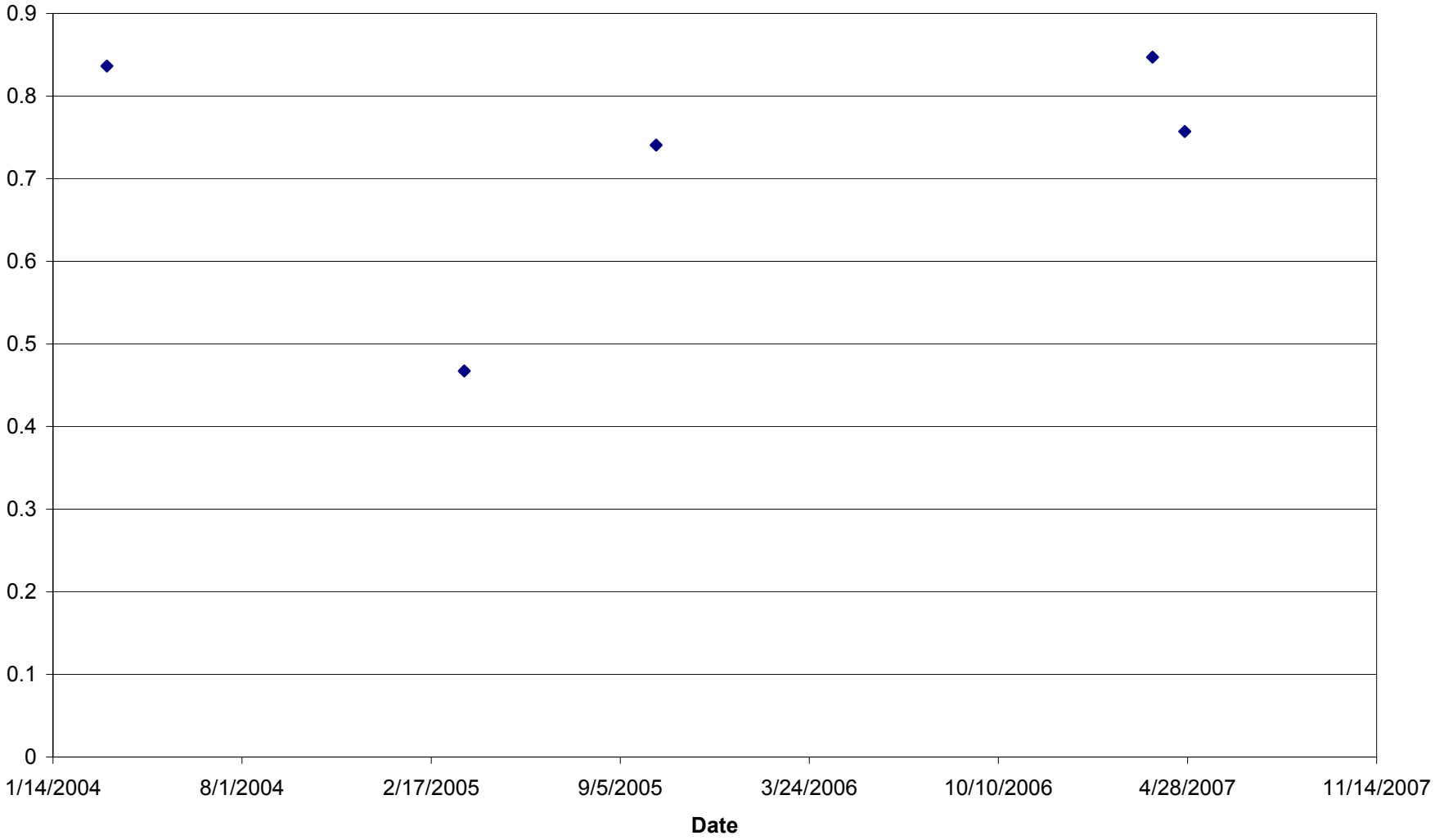
Ratio of Measured Potentially Dissolved and Total Recoverable Selenium Concentrations in the Littleton Englewood WWTP Effluent



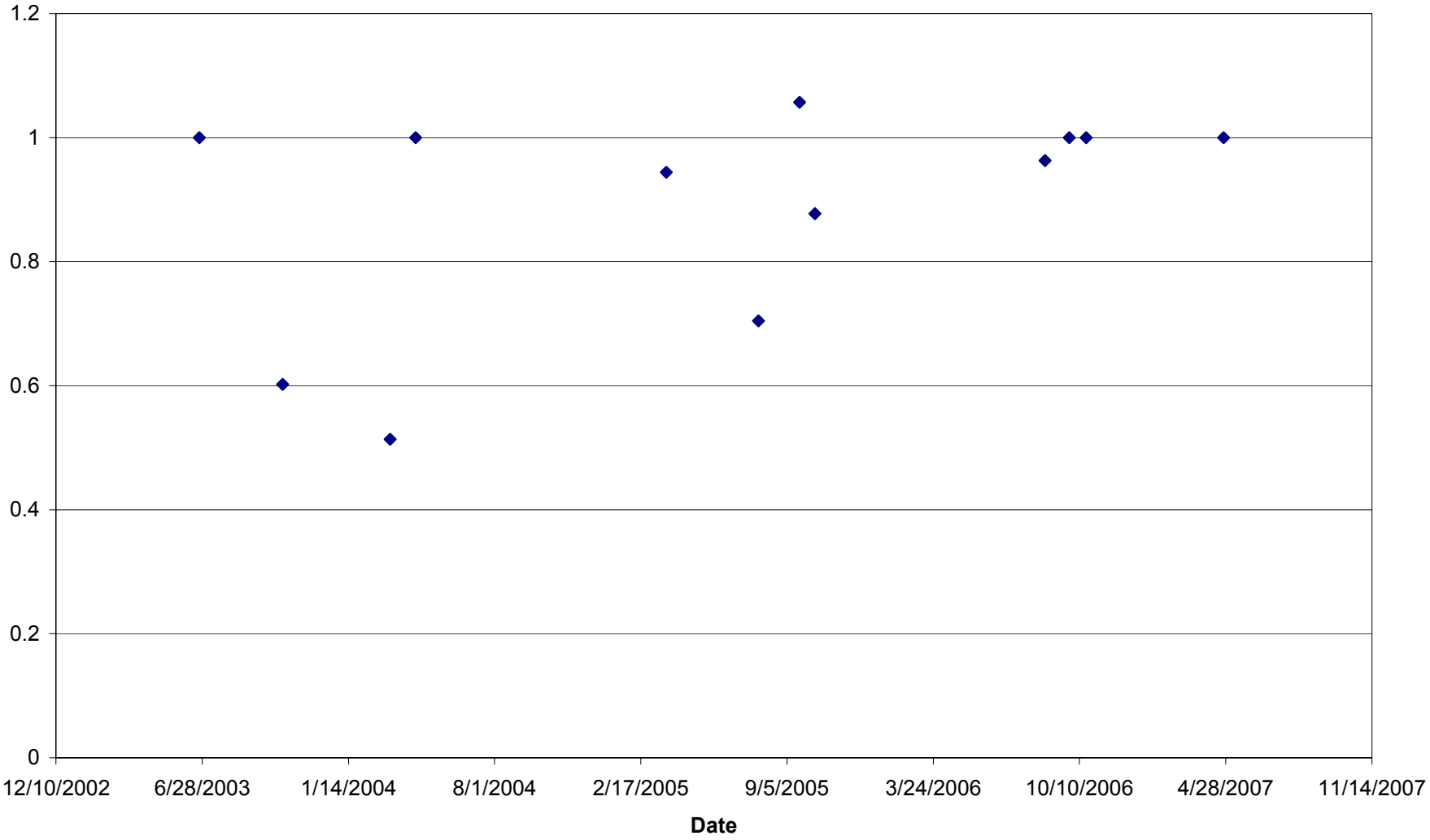
Ratio of Measured Potentially Dissolved and Total Recoverable Zinc Concentrations in the Littleton Englewood WWTP Effluent



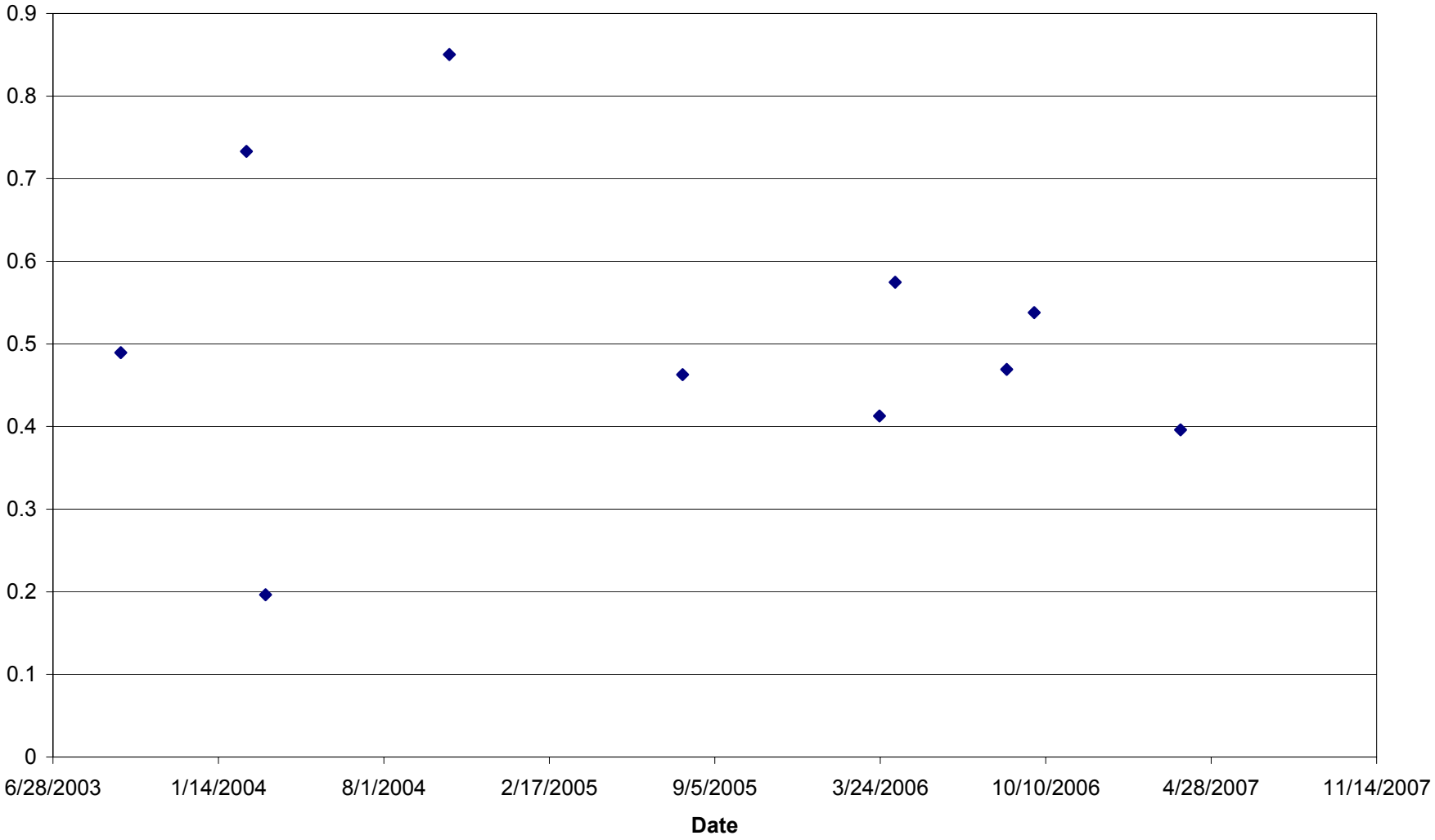
Ratio of Measured Potentially Dissolved and Total Recoverable Arsenic Concentrations in the City of Pueblo WWTP Effluent



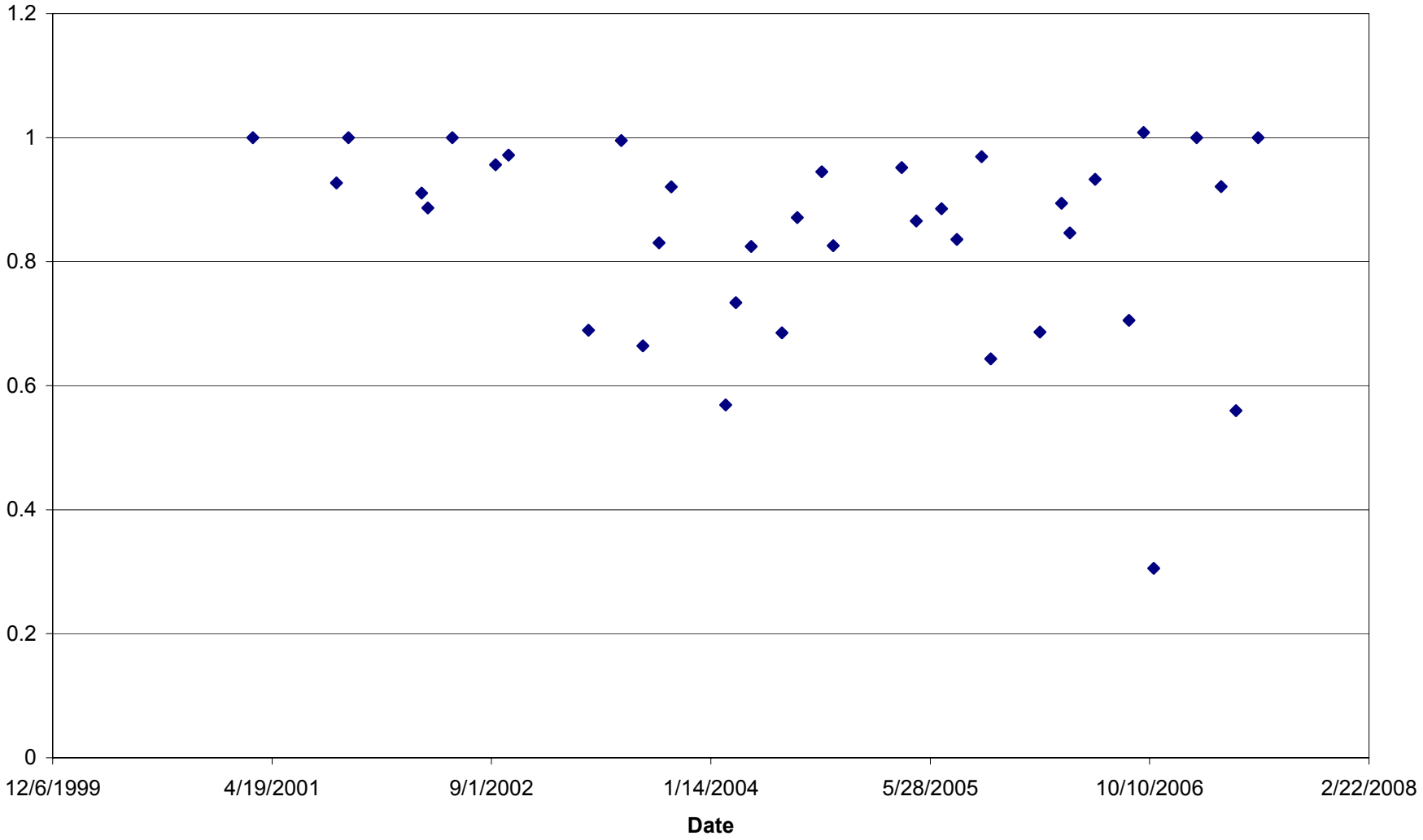
Ratio of Measured Potentially Dissolved and Total Recoverable Cadmium Concentrations in the City of Pueblo WWTP Effluent



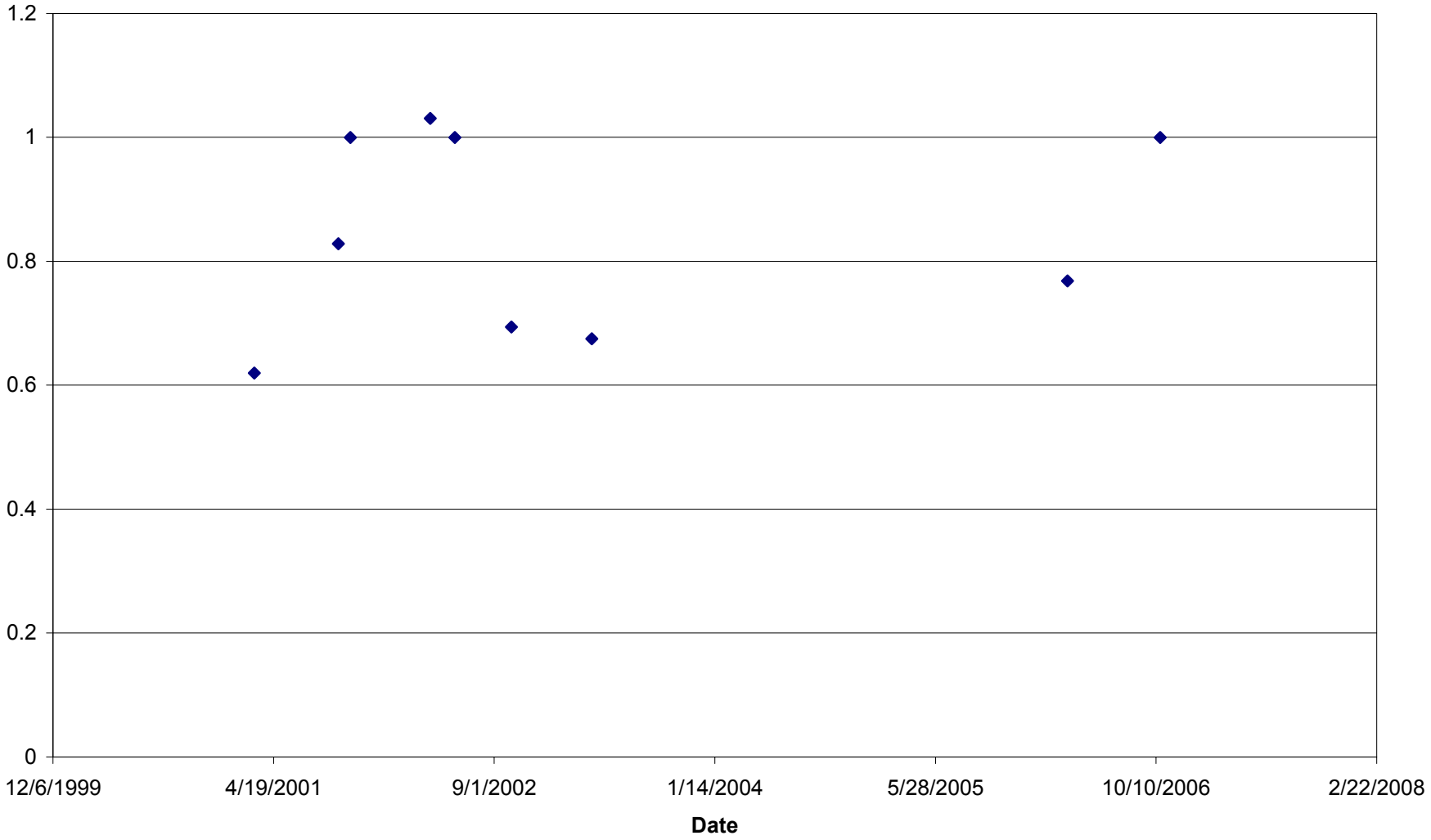
Ratio of Measured Potentially Dissolved and Total Recoverable Chromium Concentrations in the City of Pueblo WWTP Effluent



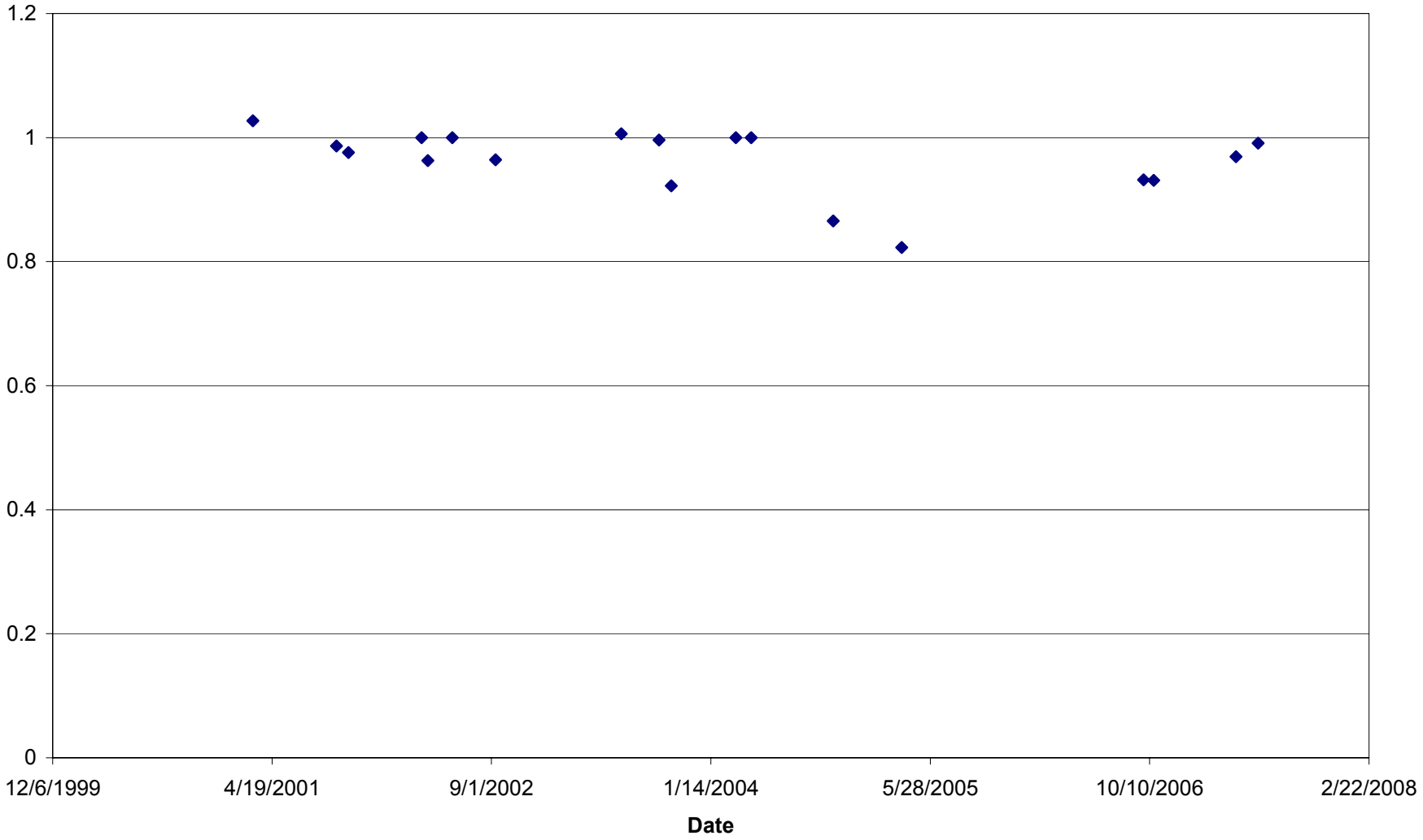
Ratio of Measured Potentially Dissolved and Total Recoverable Copper Concentrations in the City of Pueblo WWTP Effluent



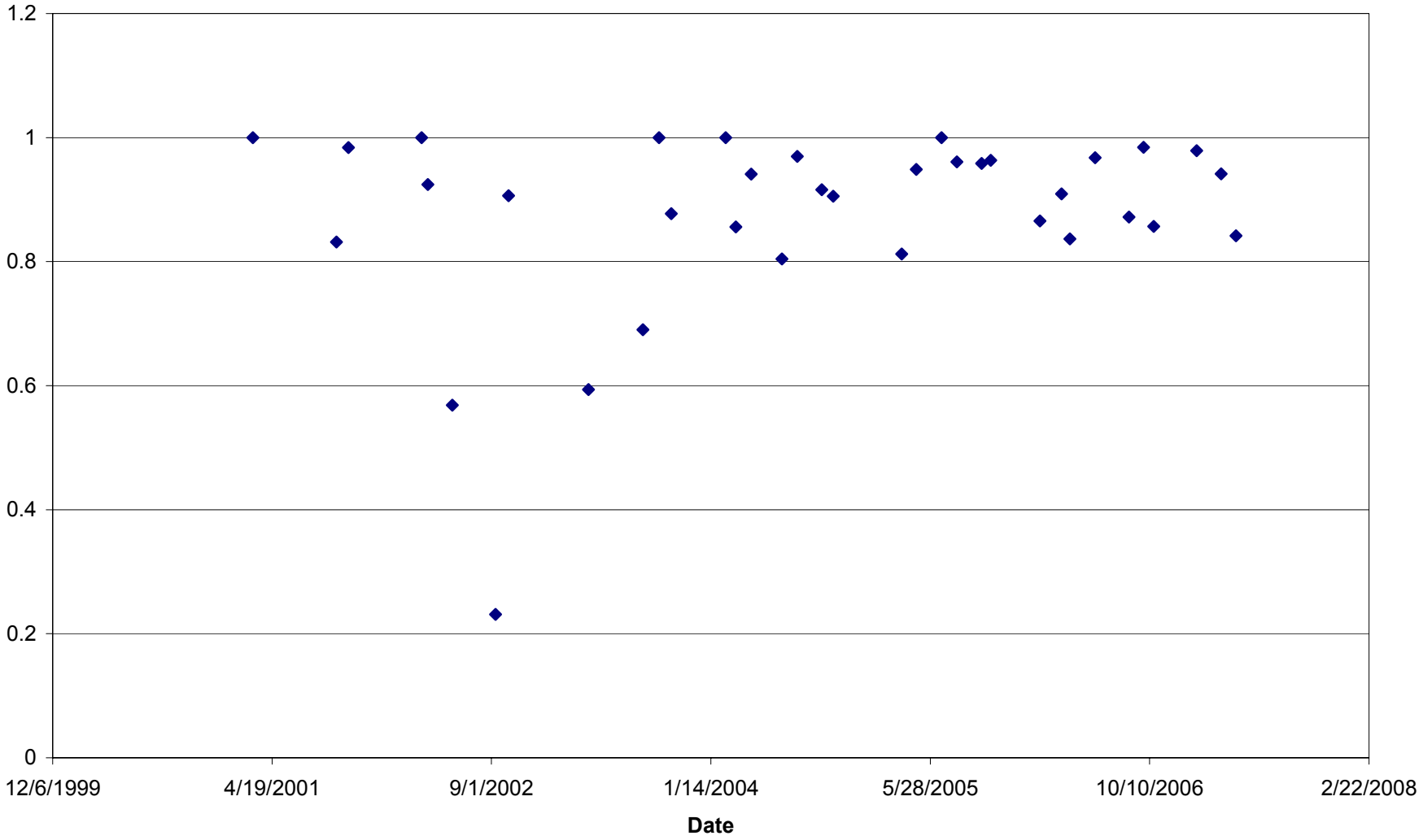
Ratio of Measured Potentially Dissolved and Total Recoverable Lead Concentrations in the City of Pueblo WWTP Effluent



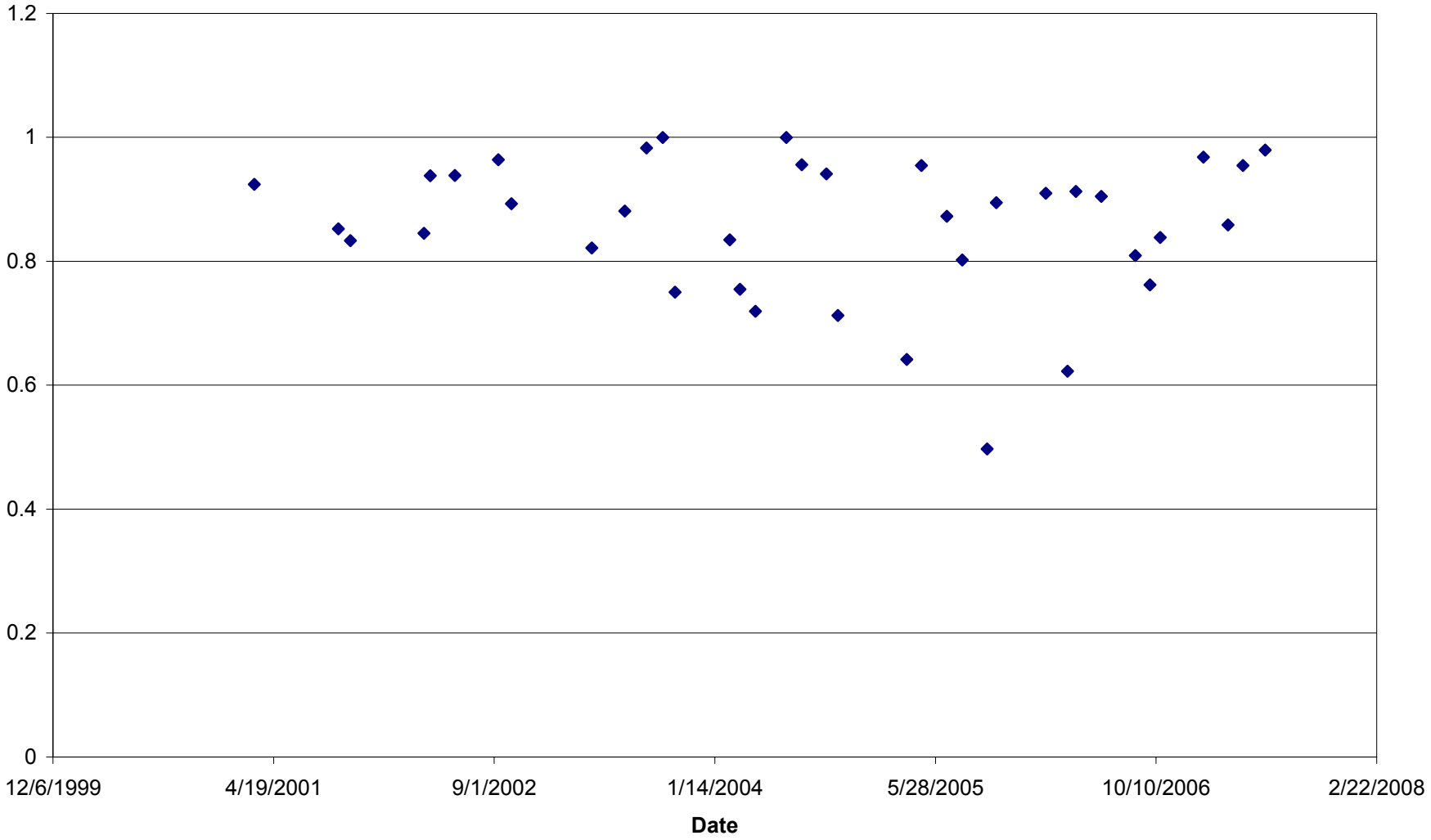
Ratio of Measured Potentially Dissolved and Total Recoverable Manganese Concentrations in the City of Pueblo WWTP Effluent



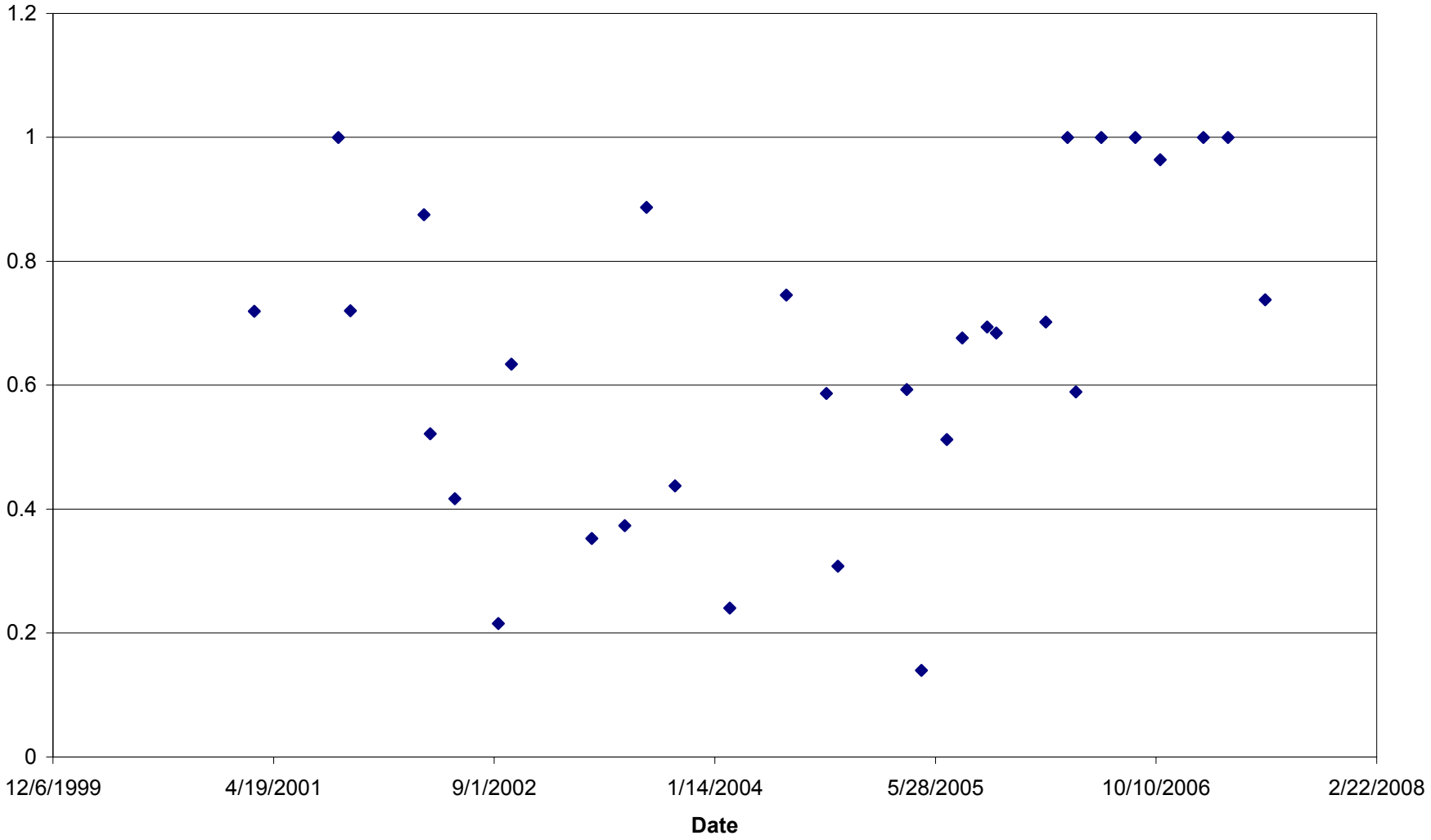
Ratio of Measured Potentially Dissolved and Total Recoverable Nickel Concentrations in the City of Pueblo WWTP Effluent



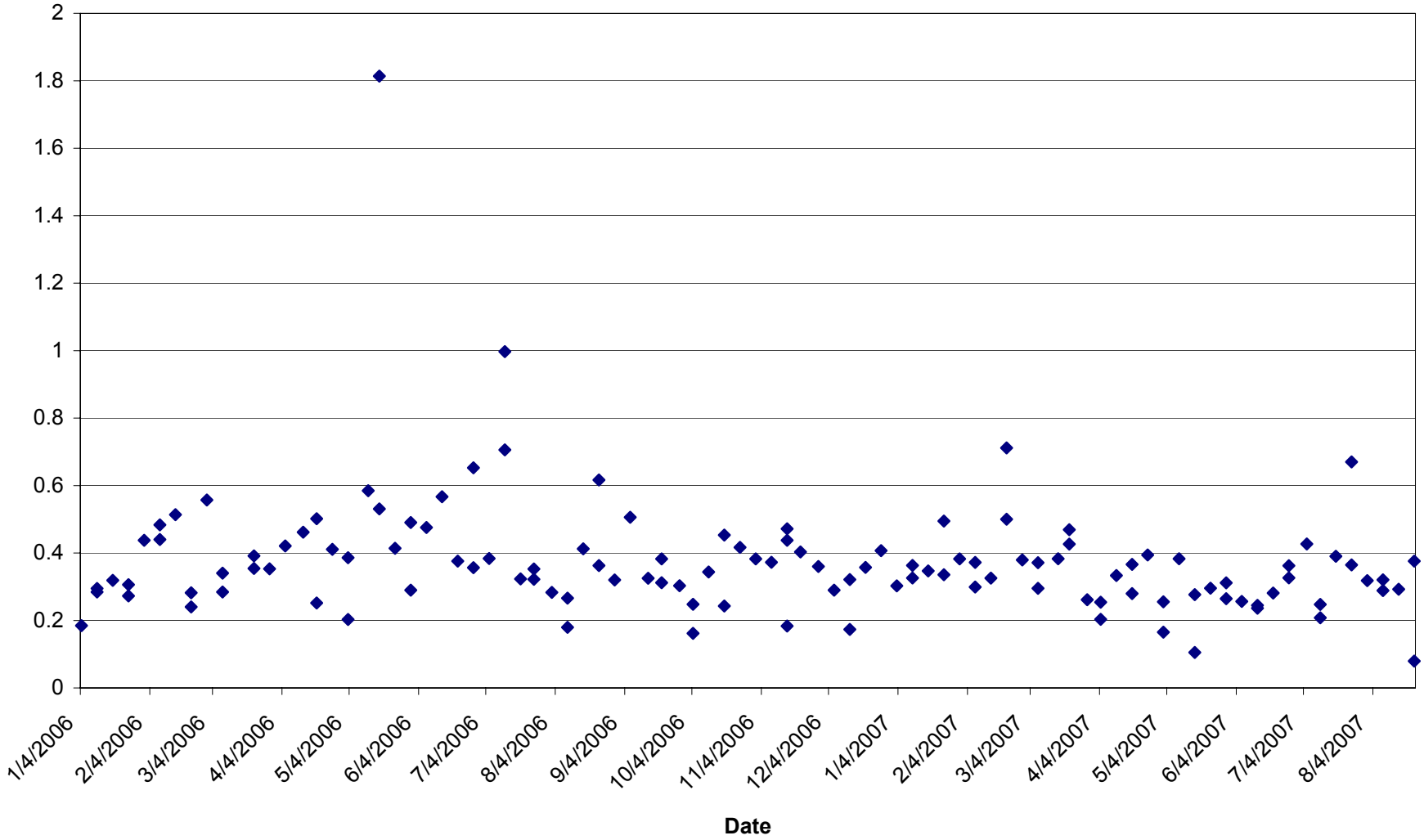
Ratio of Measured Potentially Dissolved and Total Recoverable Selenium Concentrations in the City of Pueblo WWTP Effluent

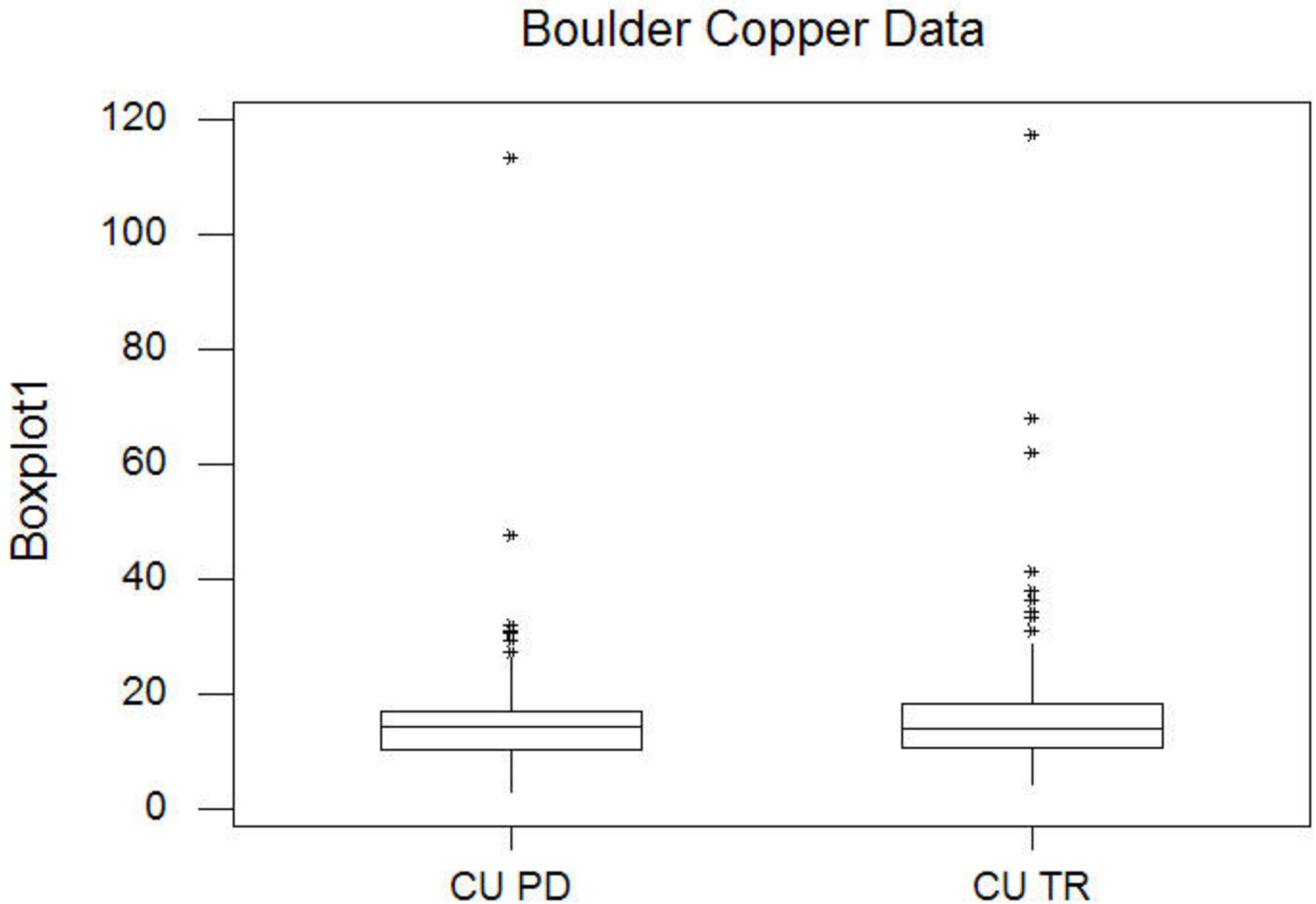


Ratio of Measured Potentially Dissolved and Total Recoverable Silver Concentrations in the City of Pueblo WWTP Effluent



Ratio of Measured Potentially Dissolved and Total Recoverable Iron Concentrations in Xcel's Effluent (Leggett 001)




Boulder Copper Data
Boxplot1
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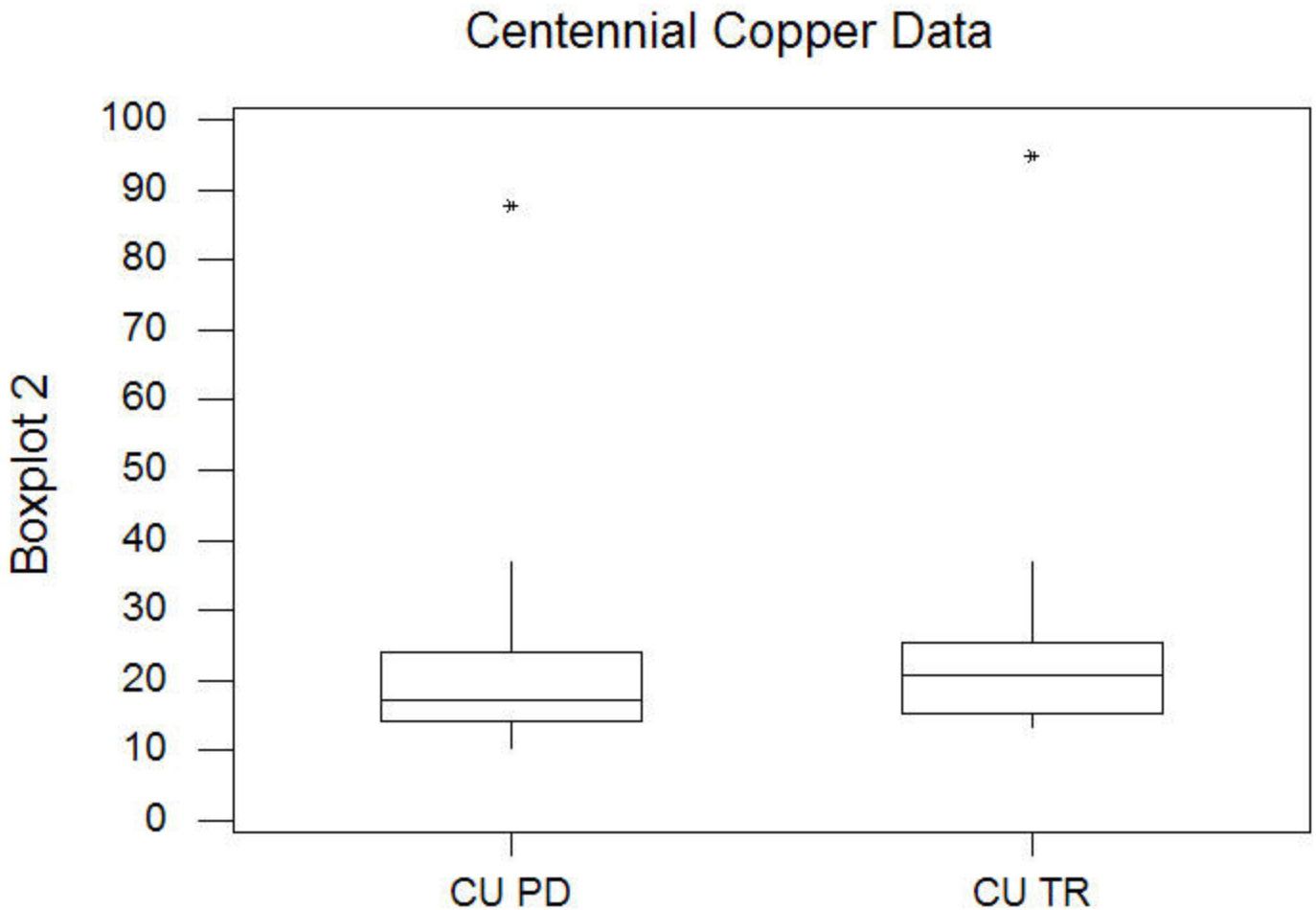
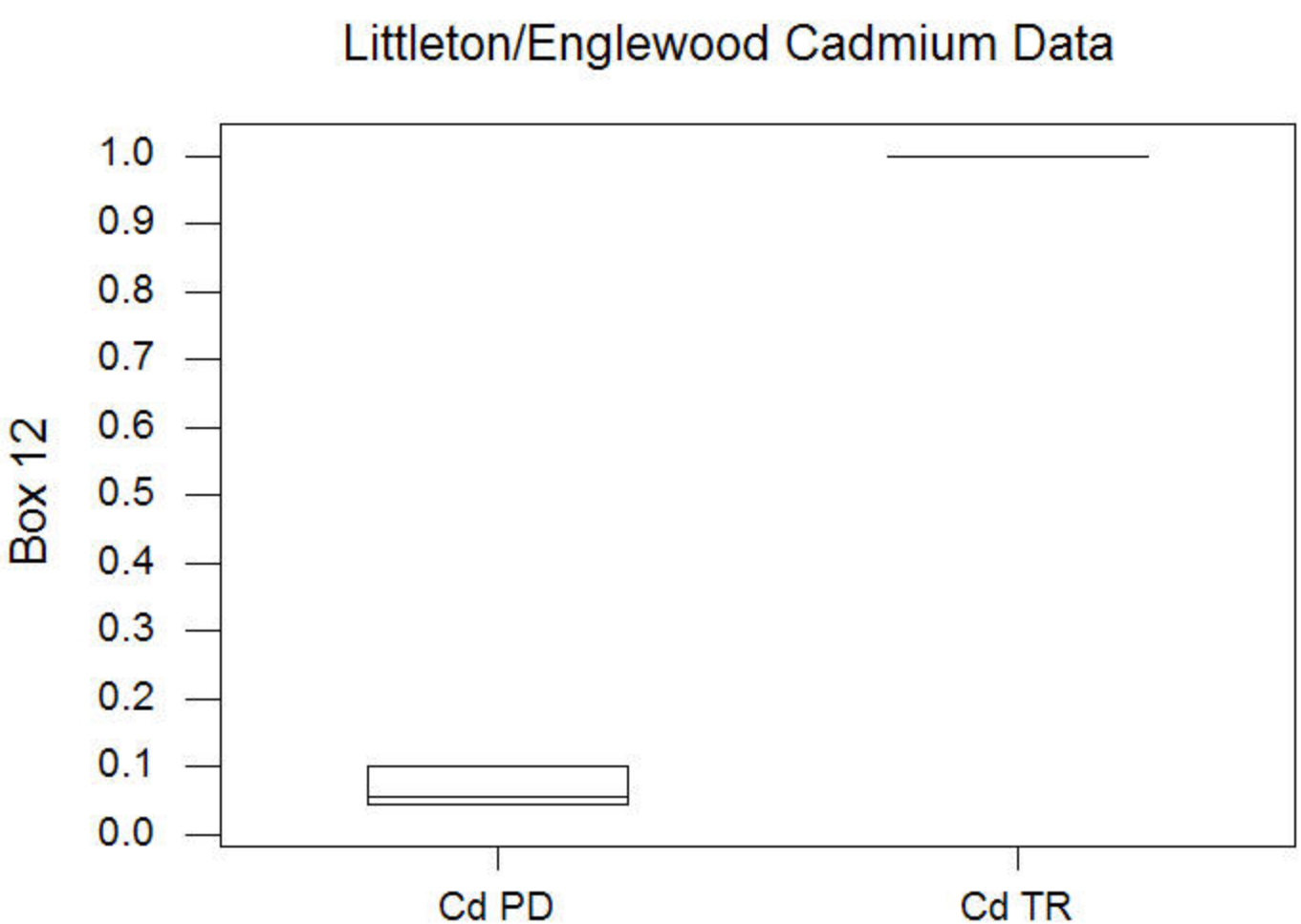
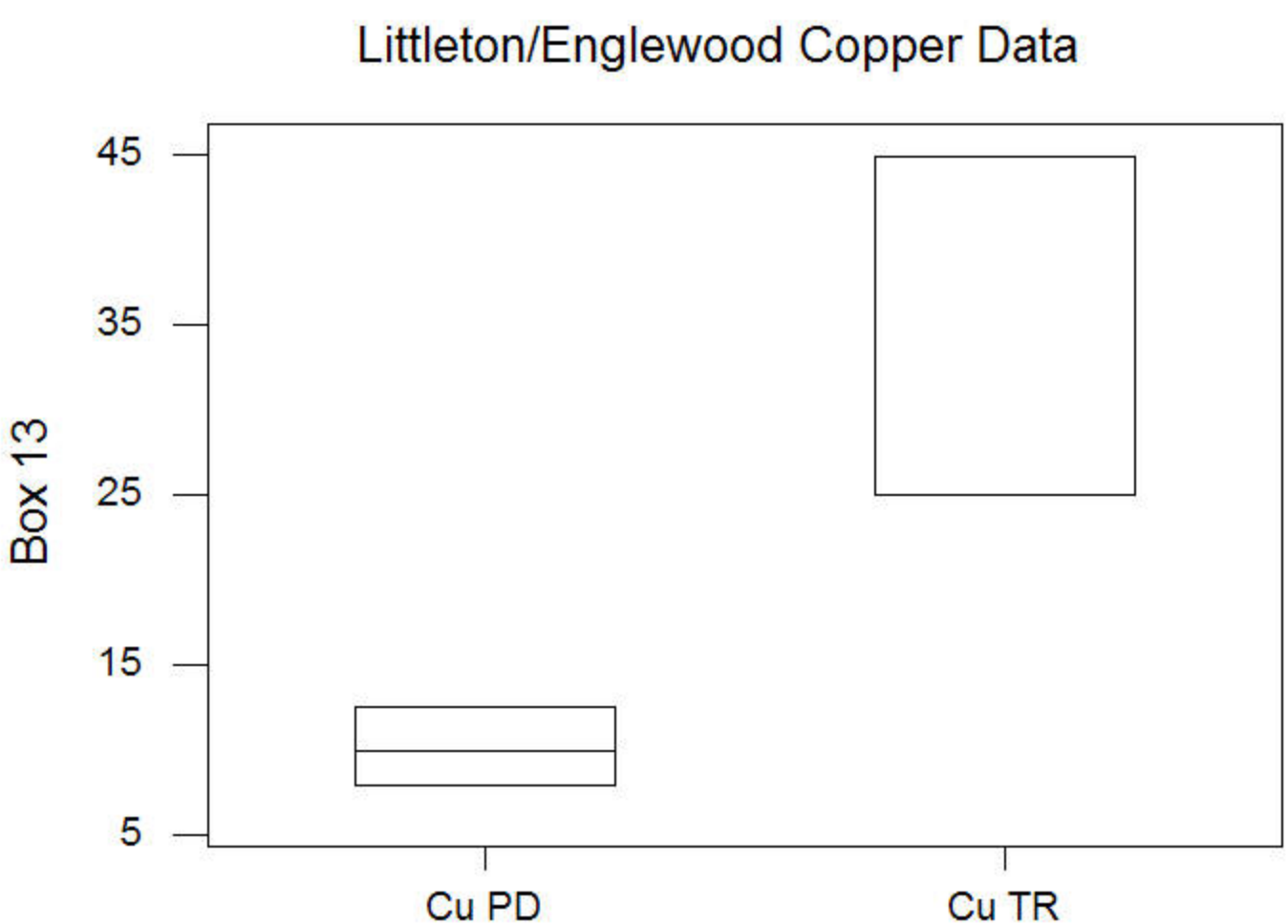
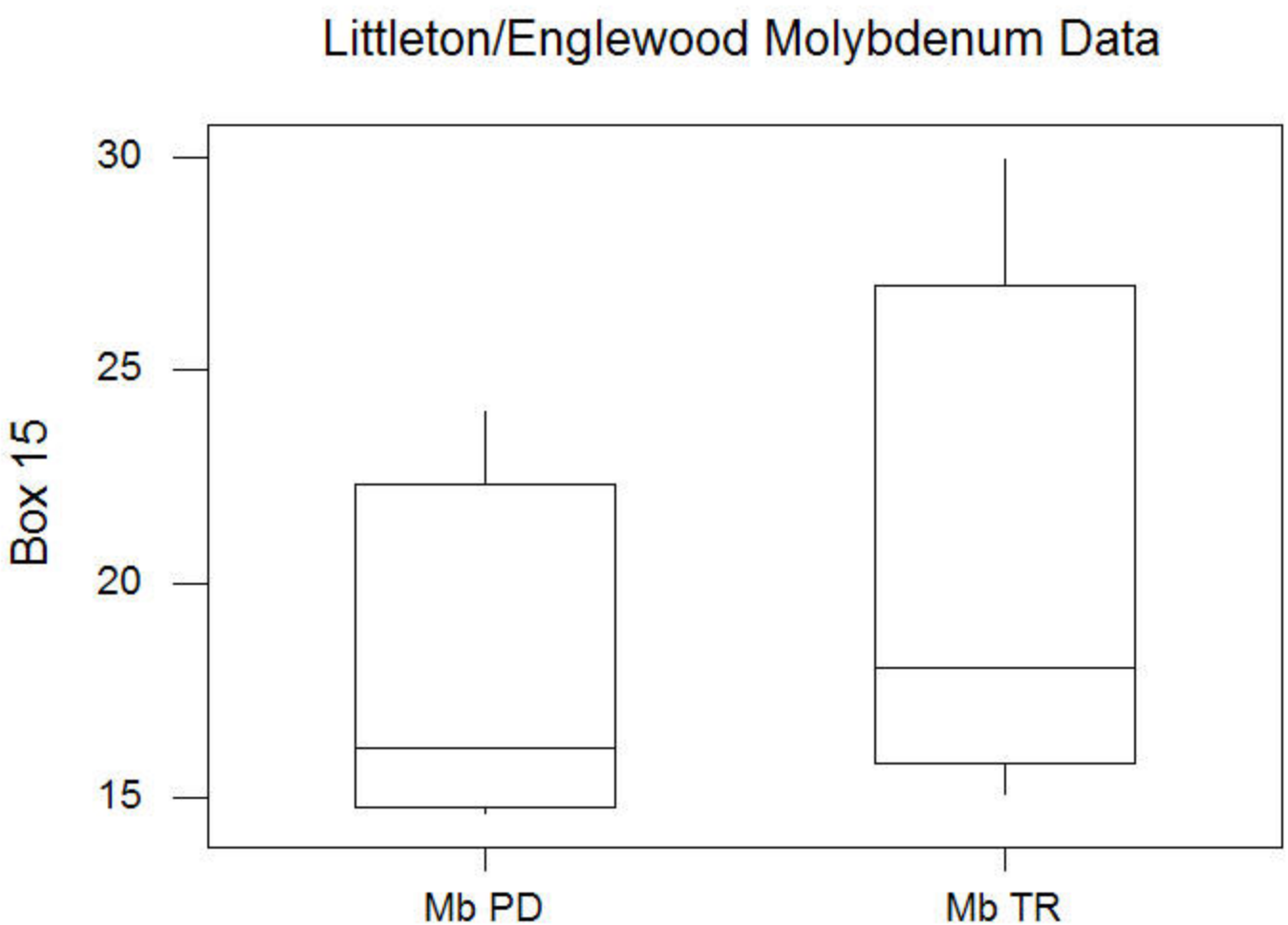
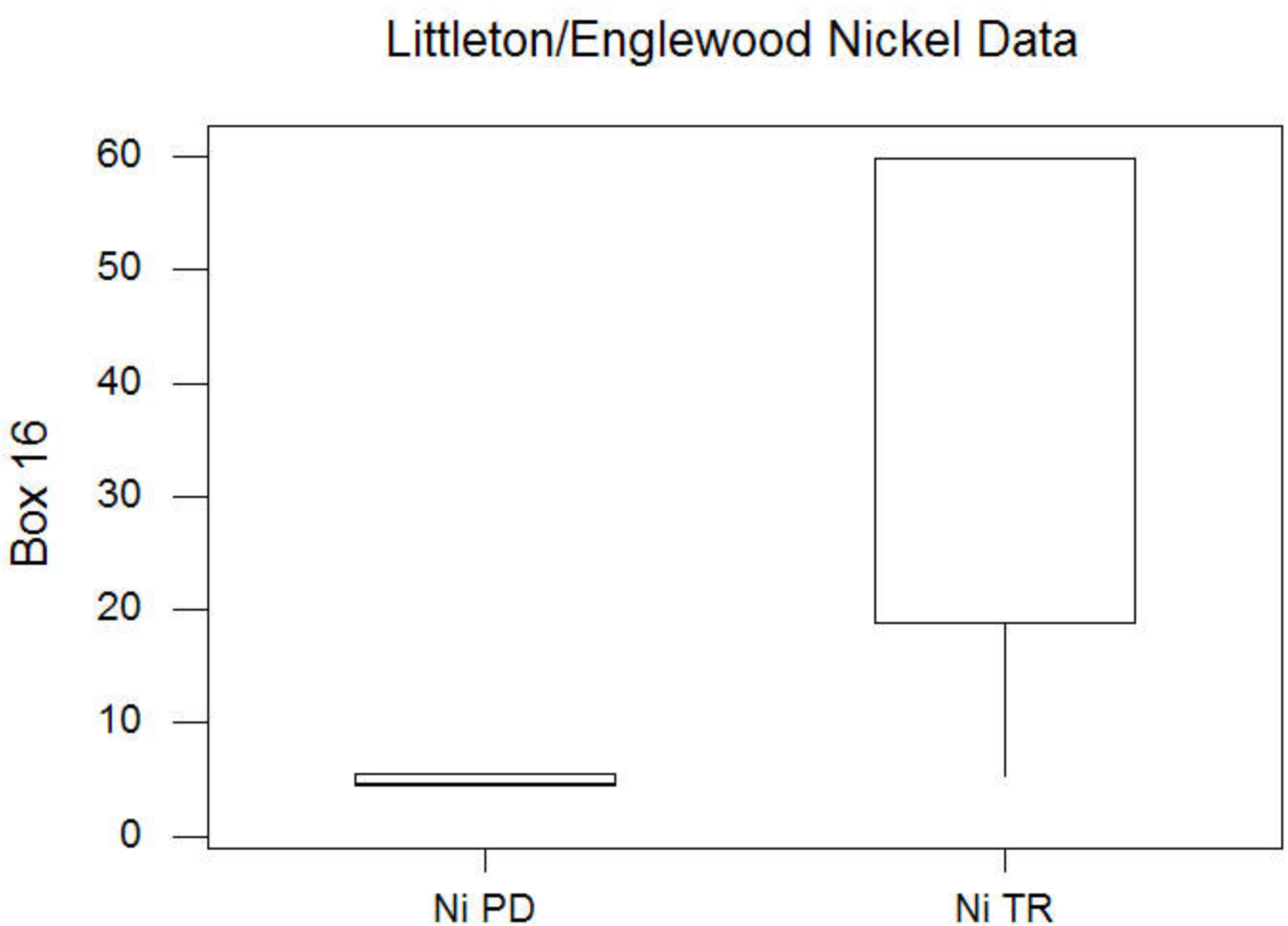
100
80
60
40
20
0
CU PD
CU TR

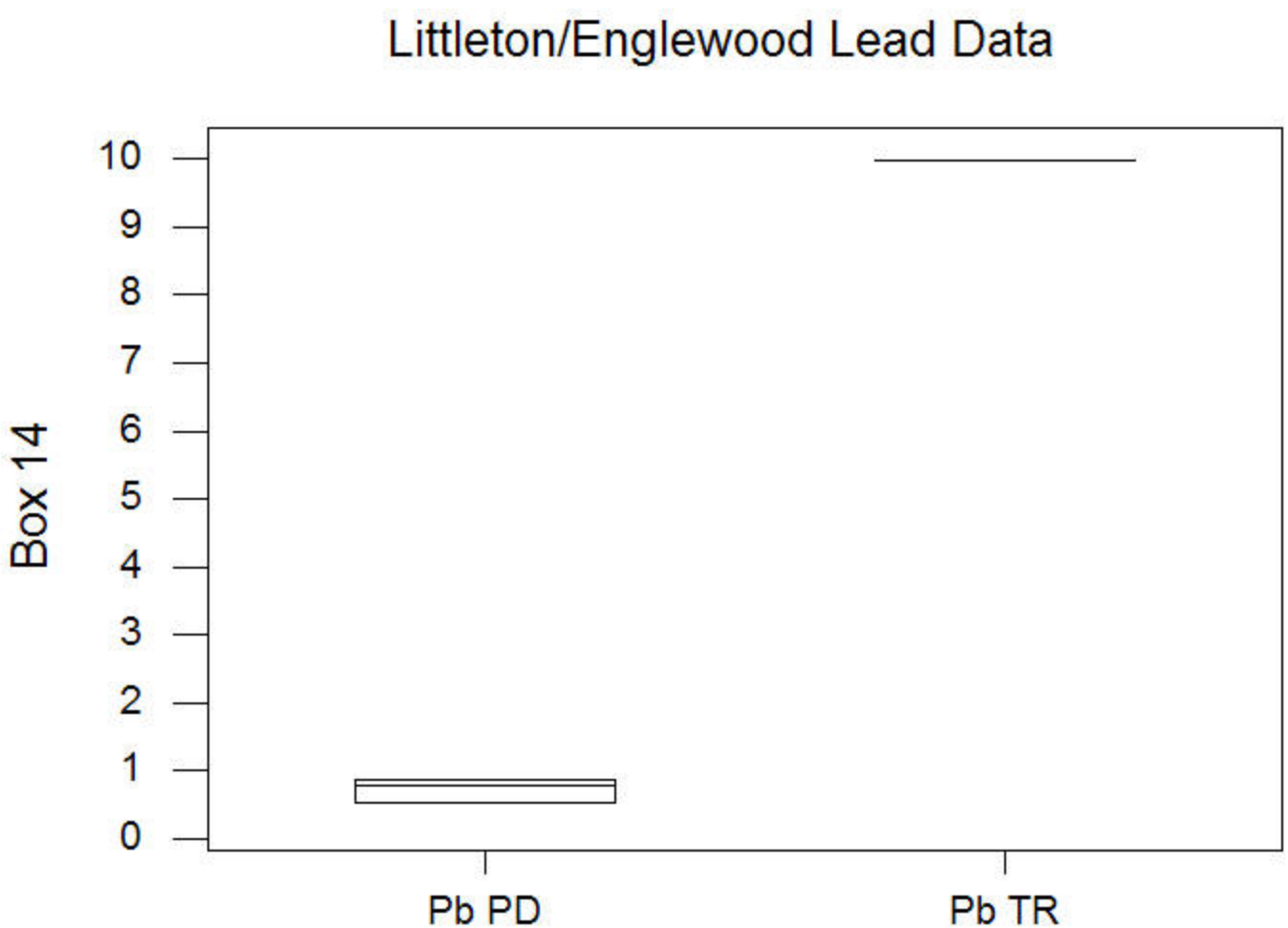

Centennial Copper Data
Boxplot 2
100
90
80
70
60
50
40
30
20
10
0
CU PD
CU TR

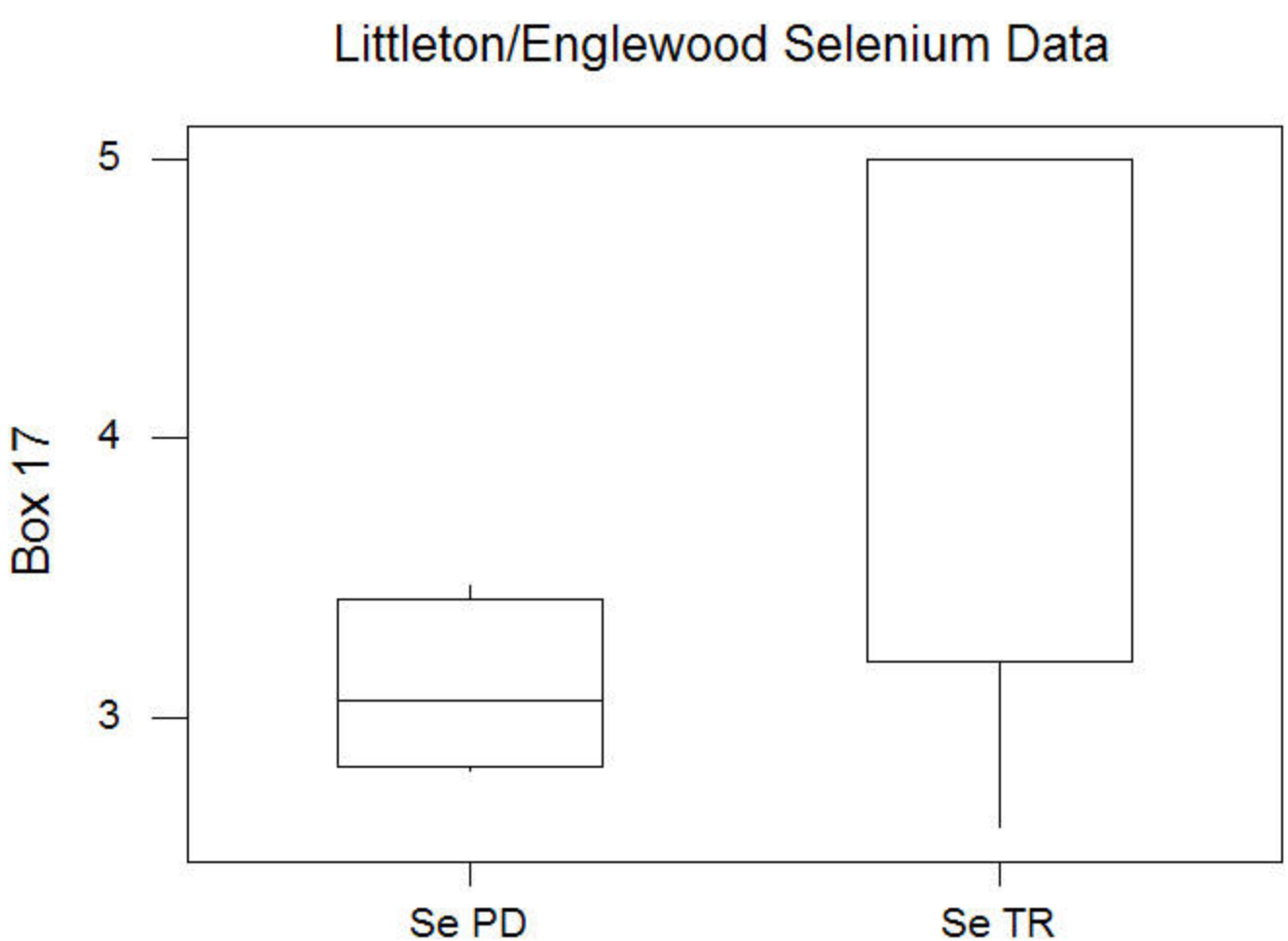

Littleton/Englewood Cadmium Data
Box 12
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Cd PD
Cd TR

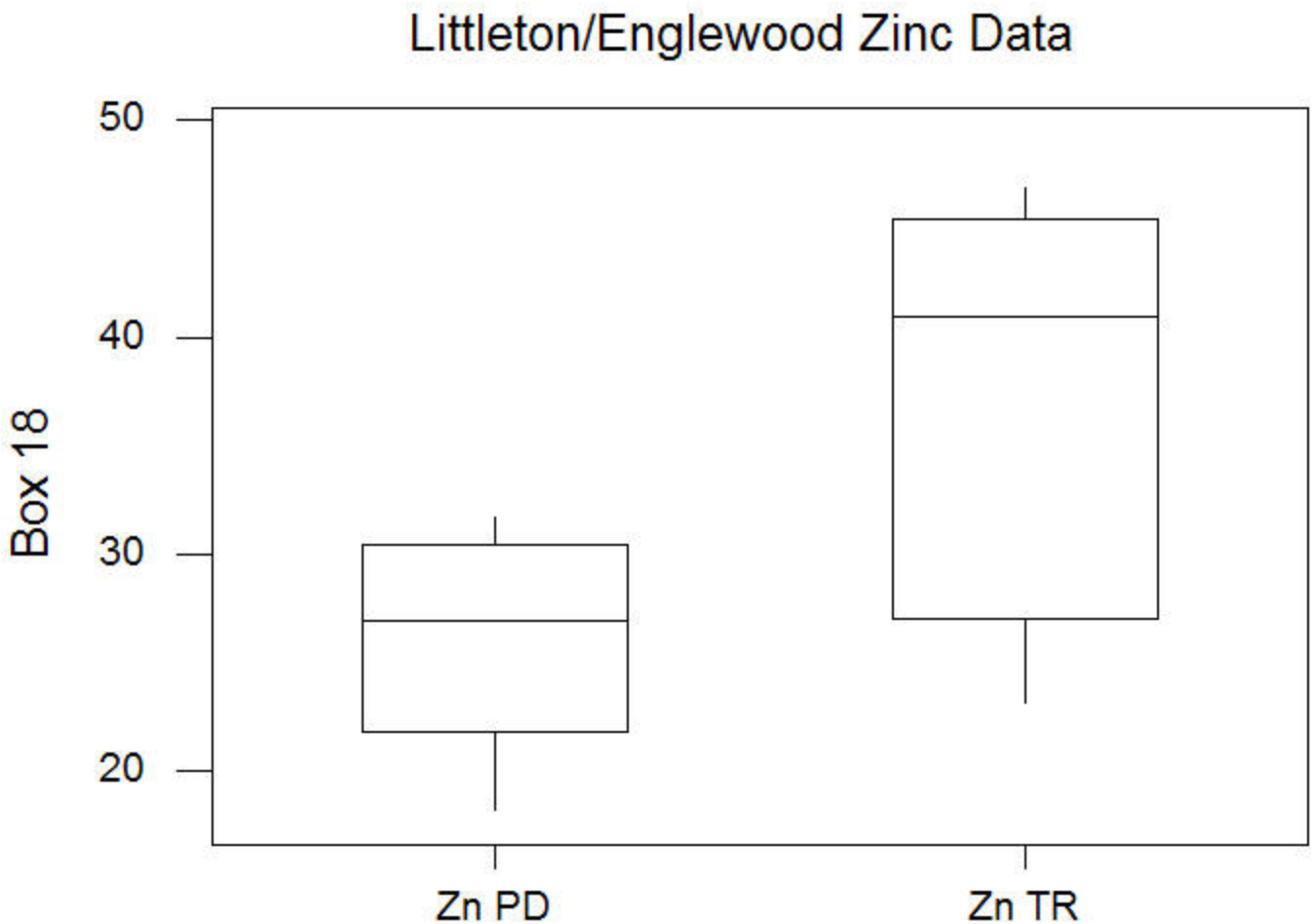

Littleton/Englewood Copper Data
Box 13
45
35
25
15
5
Cu PD
Cu TR

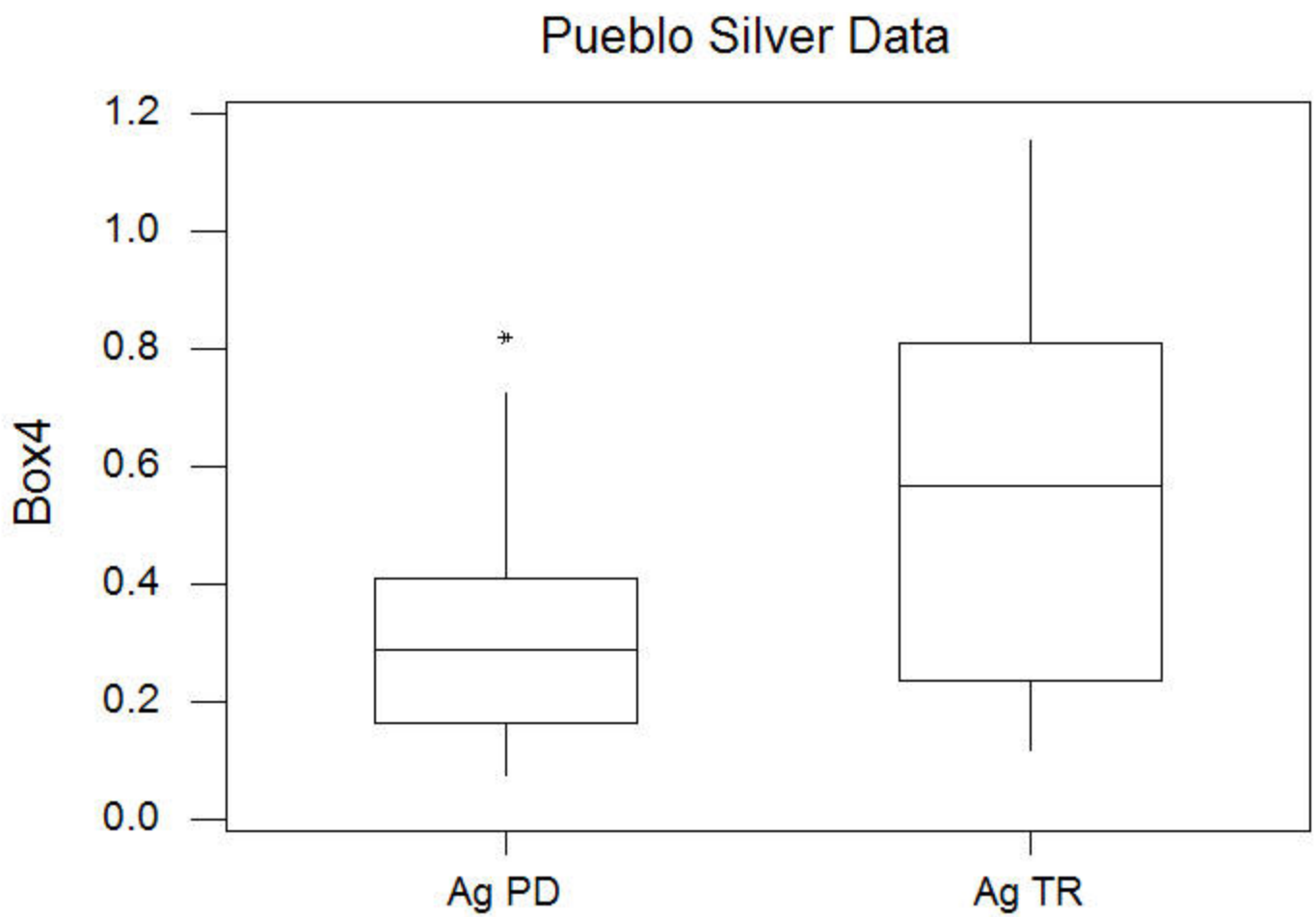

Littleton/Englewood Molybdenum Data
Box 15
30
25
20
15
Mb PD
Mb TR

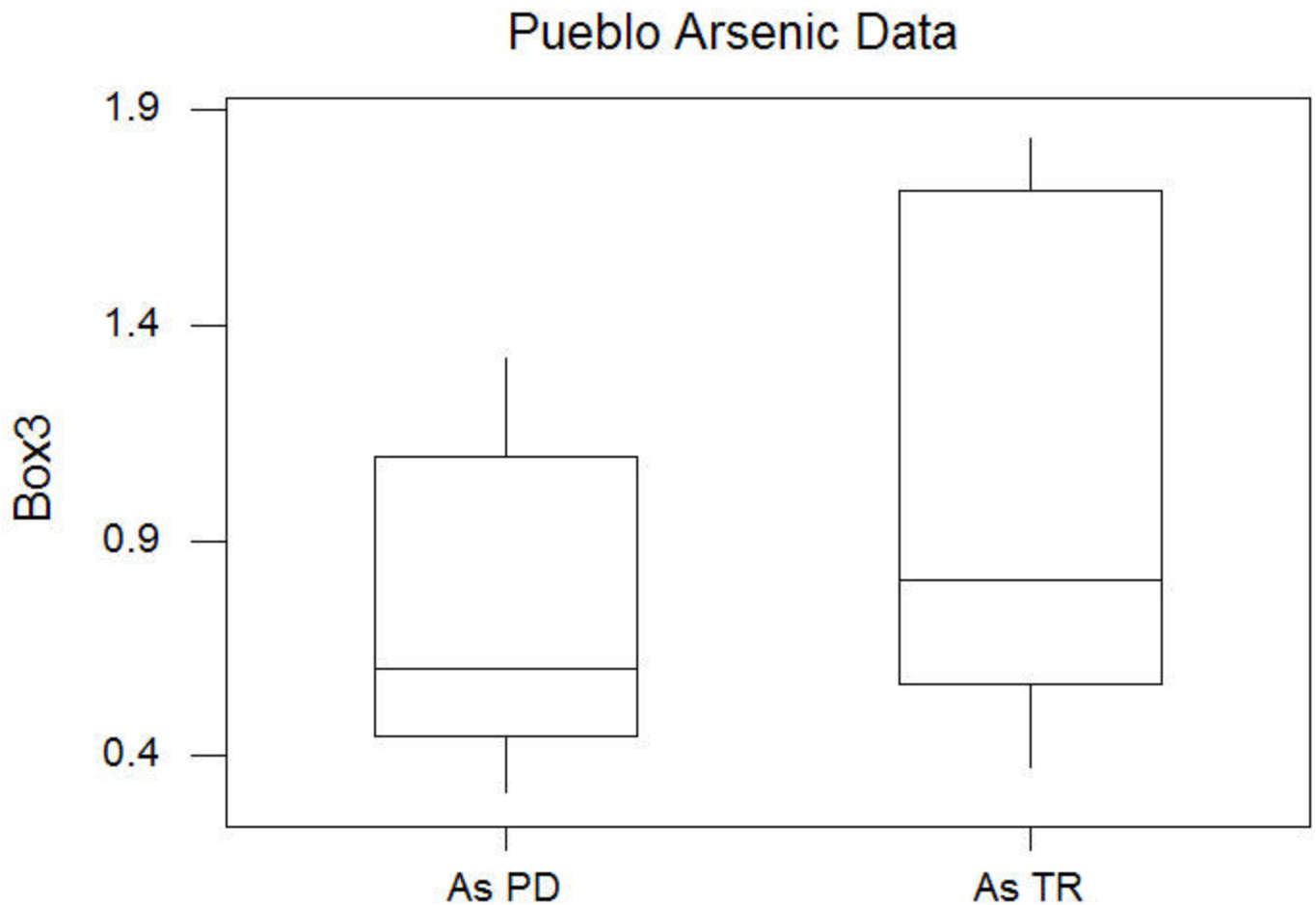

Littleton/Englewood Nickel Data
Box 16
60
50
40
30
20
10
0
Ni PD
Ni TR

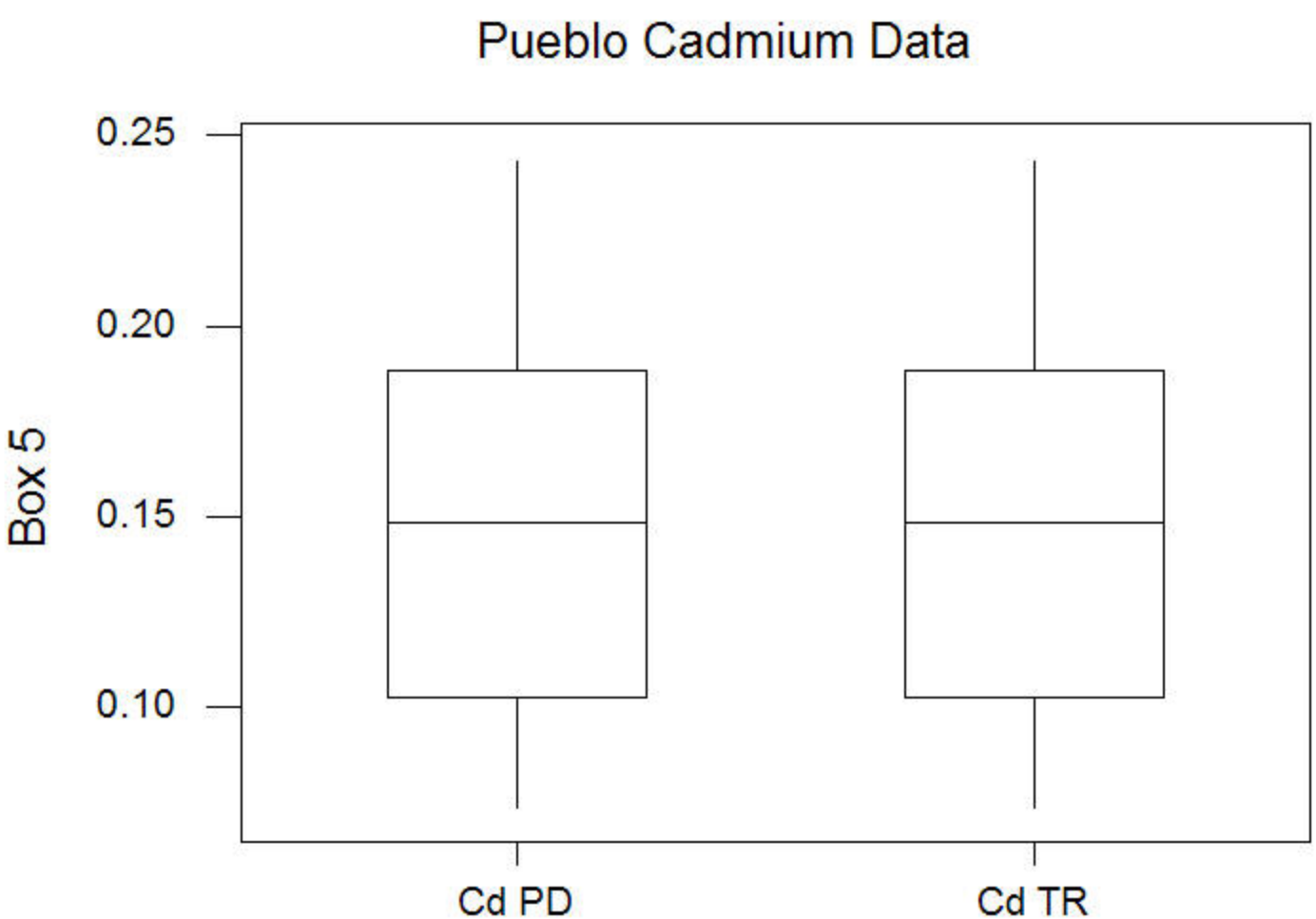

Littleton/Englewood Lead Data
Box 14
10
9
8
7
6
5
4
3
2
1
0
Pb PD
Pb TR

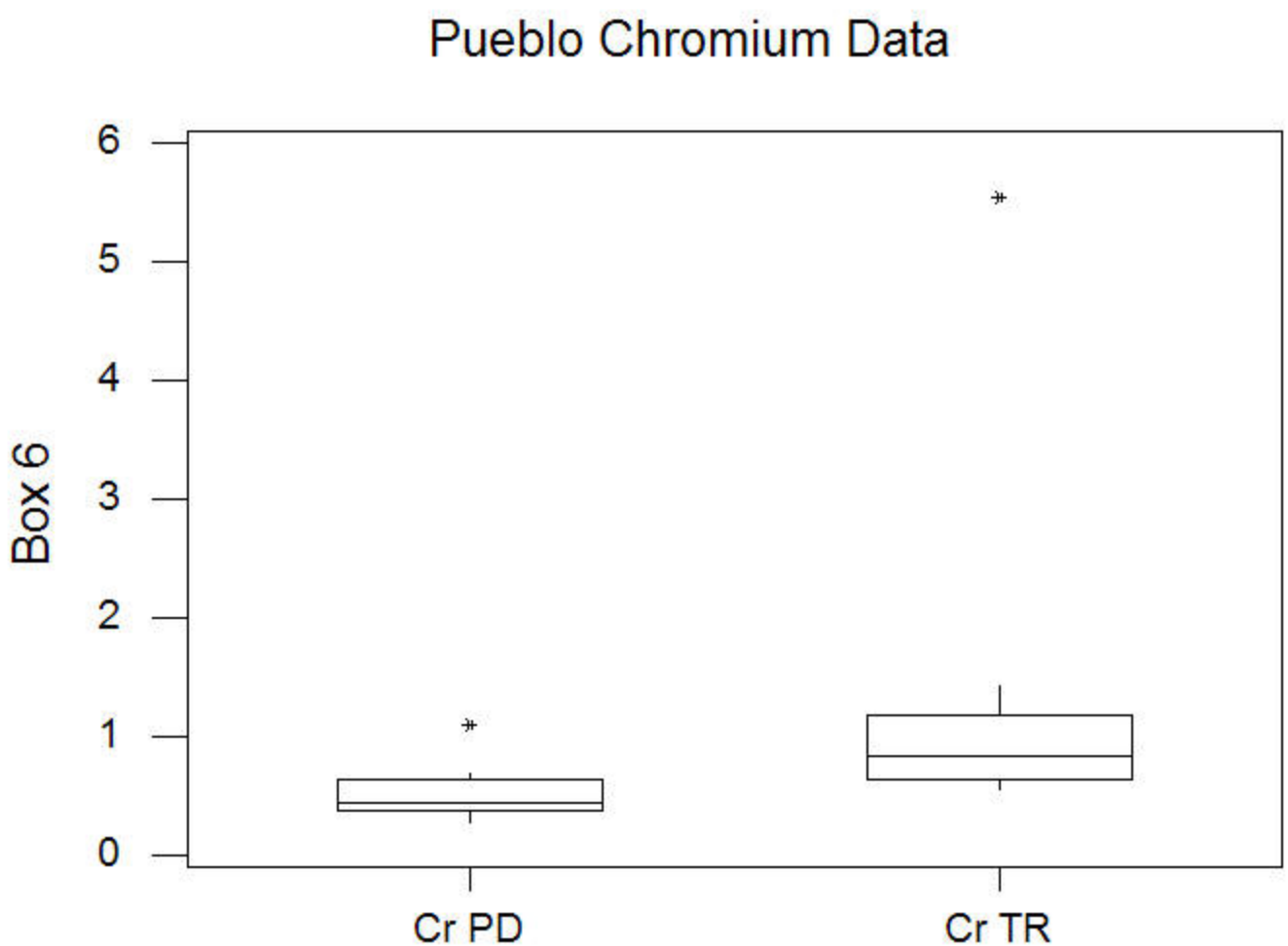

Littleton/Englewood Selenium Data
Box 17
5
4
3
Se PD
Se TR

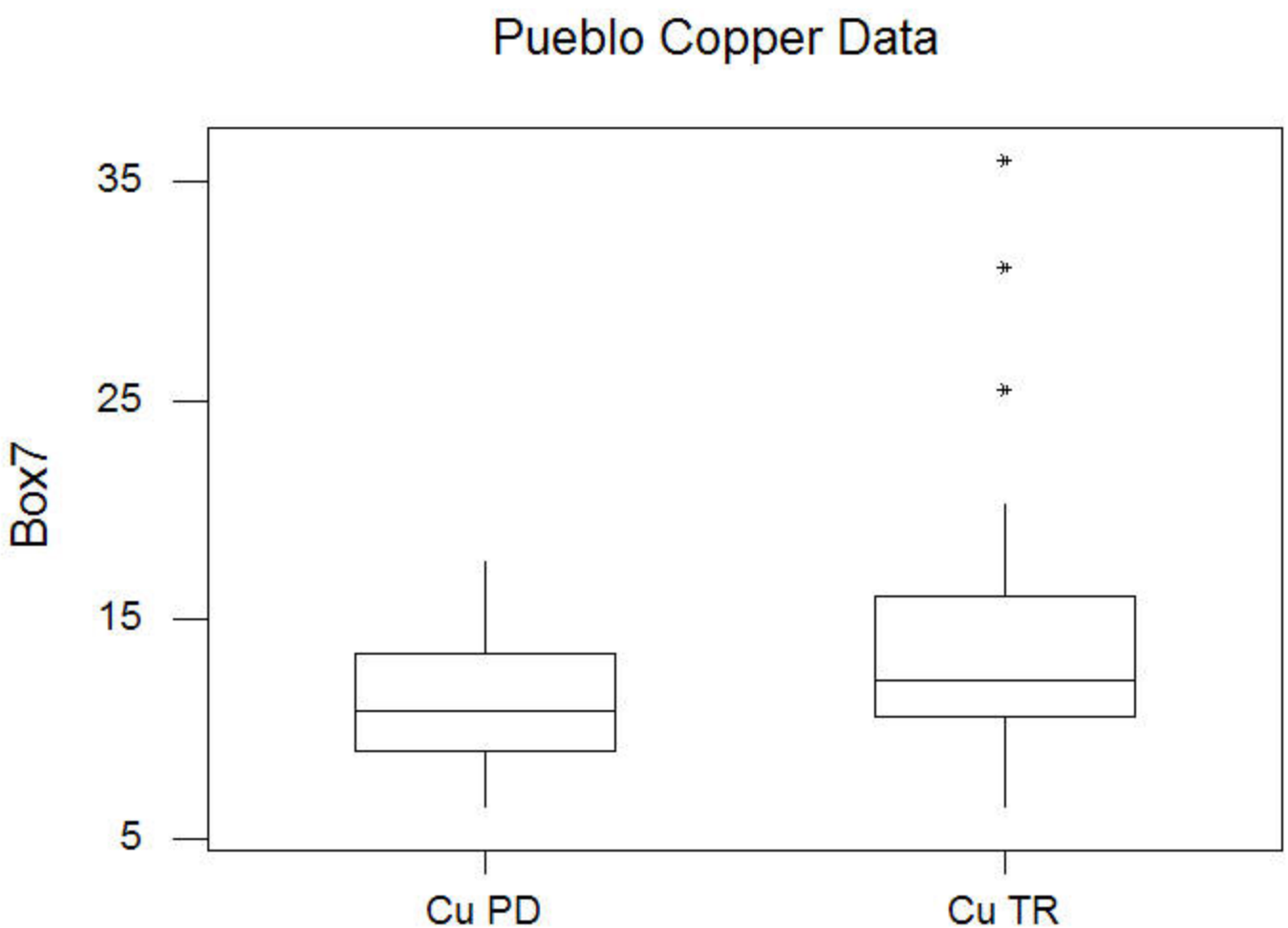

Littleton/Englewood Zinc Data
Box 18
50
40
30
20
Zn PD
Zn TR

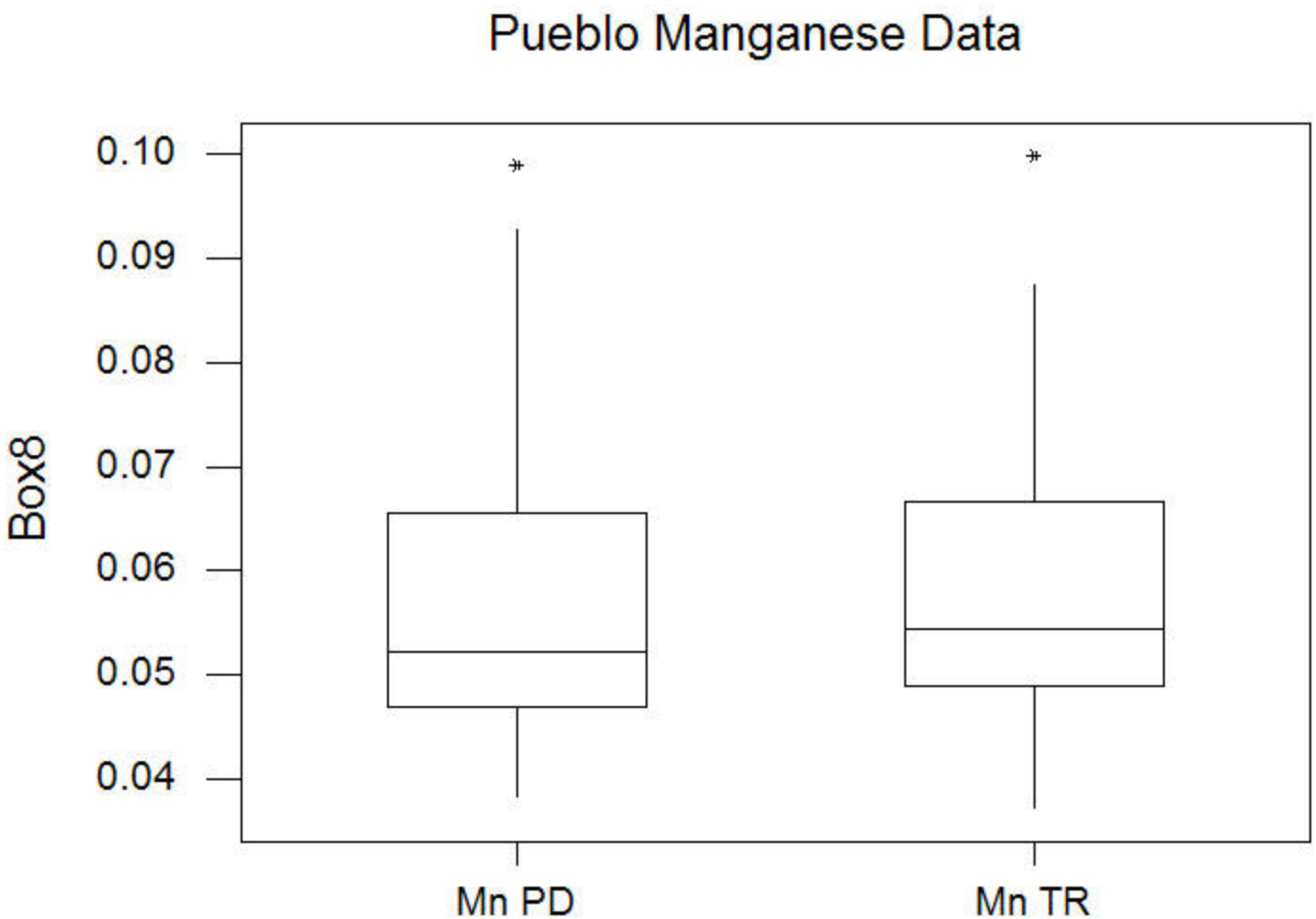

Pueblo Silver Data
Box4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Ag PD
Ag TR

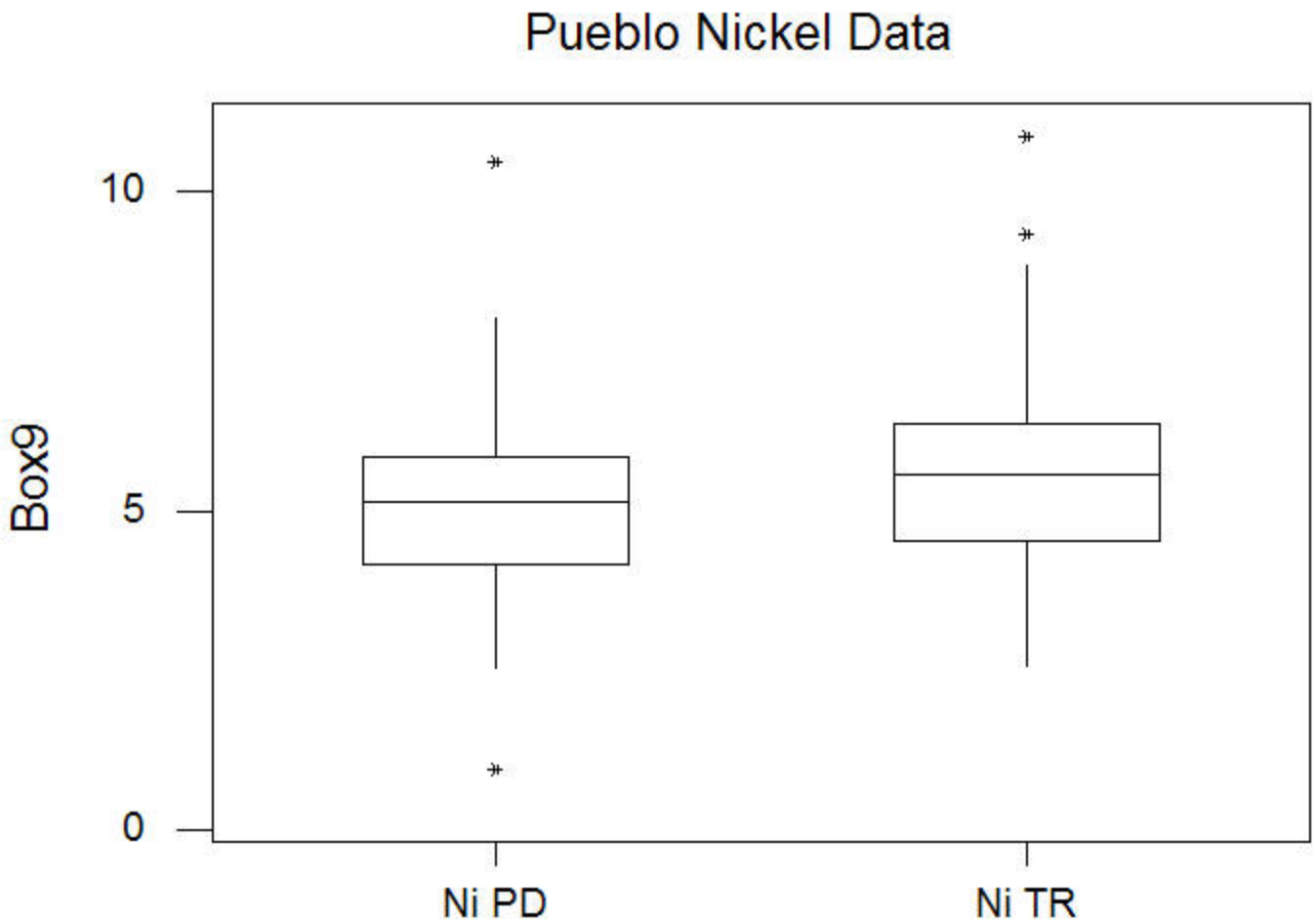

Pueblo Arsenic Data
1.9
1.4
0.9
0.4
Box3
As PD
As TR

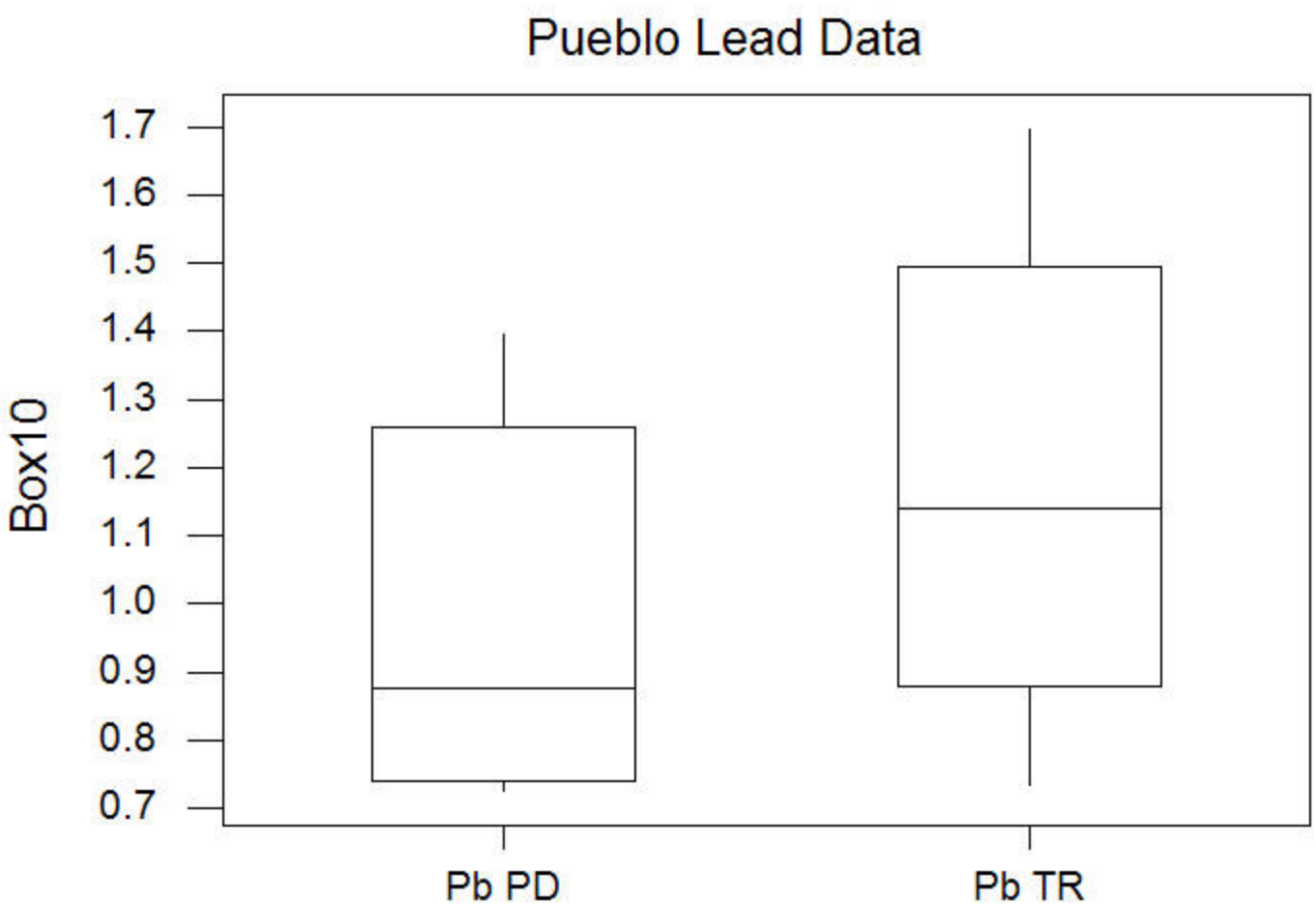

Pueblo Cadmium Data
0.25
0.20
0.15
0.10
Box 5
Cd PD
Cd TR

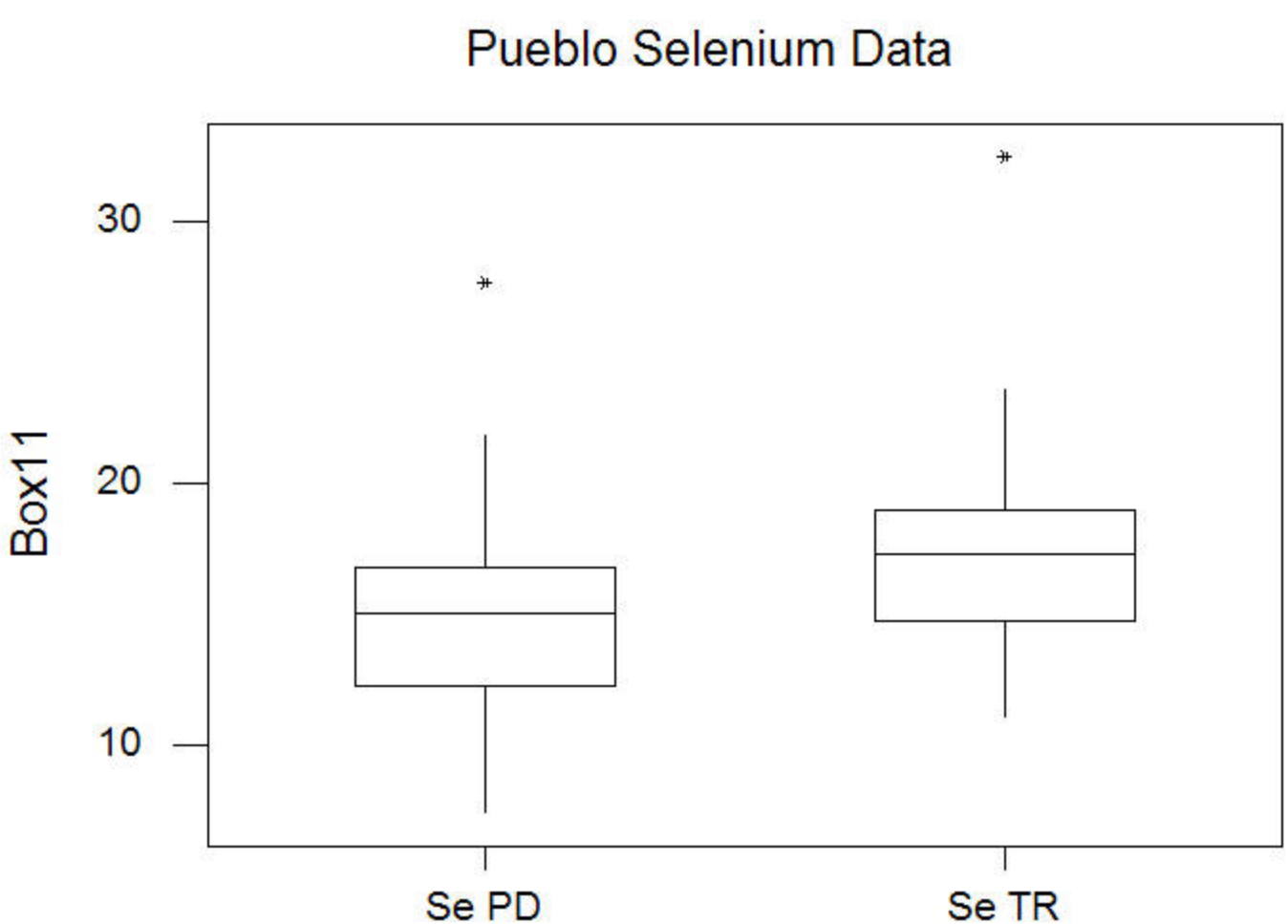

Pueblo Chromium Data
Box 6
6
5
4
3
2
1
0
Cr PD
Cr TR

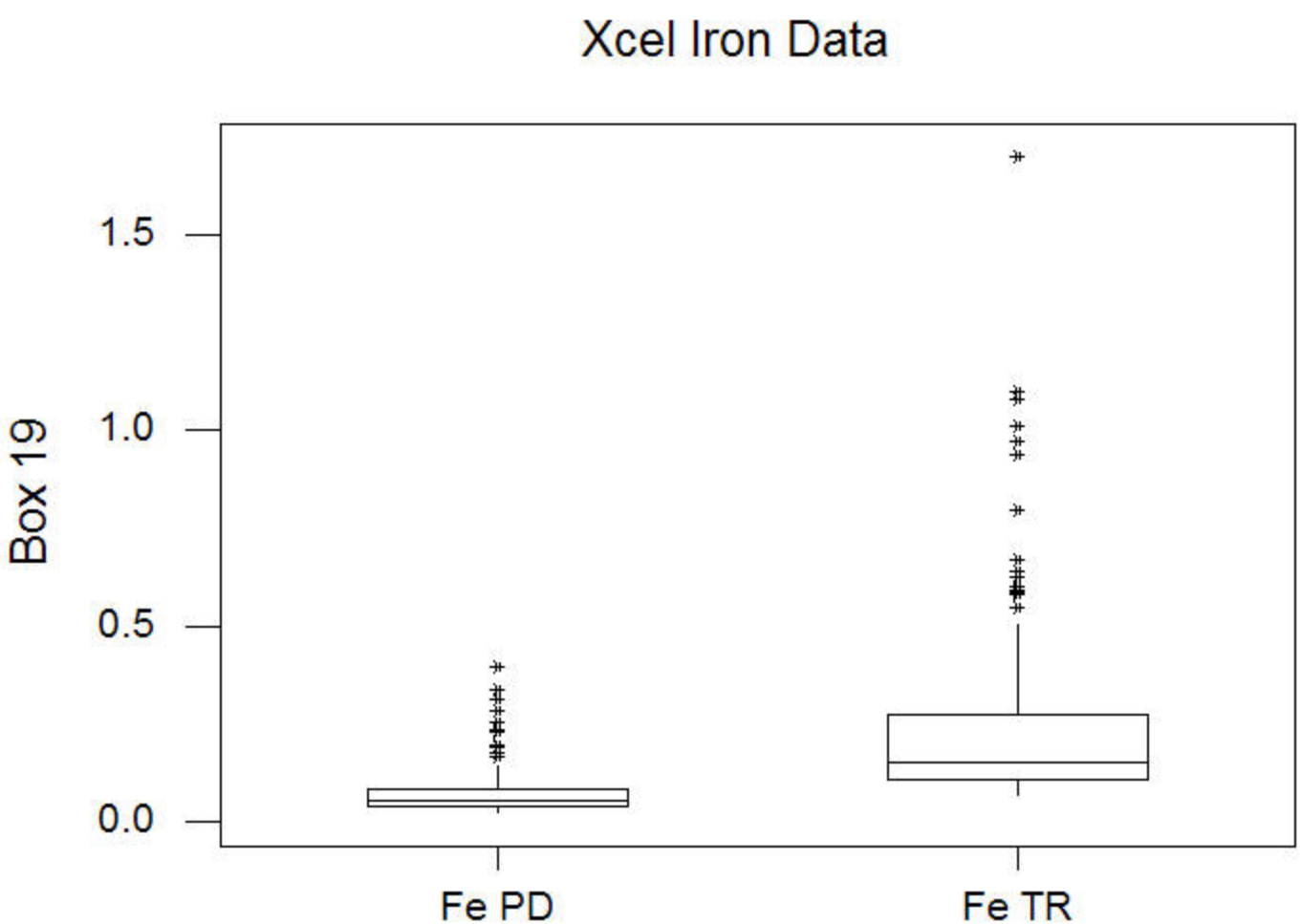

Pueblo Copper Data
Box7
35
25
15
5
Cu PD
Cu TR


Pueblo Manganese Data
Box8
0.10
0.09
0.08
0.07
0.06
0.05
0.04
Mn PD
Mn TR


Pueblo Nickel Data
Box9
10
5
0
Ni PD
Ni TR


Pueblo Lead Data
Box10
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
Pb PD
Pb TR


Pueblo Selenium Data
Box11
30
20
10
Se PD
Se TR


Xcel Iron Data
Box 19
1.5
1.0
0.5
0.0
Fe PD
Fe TR