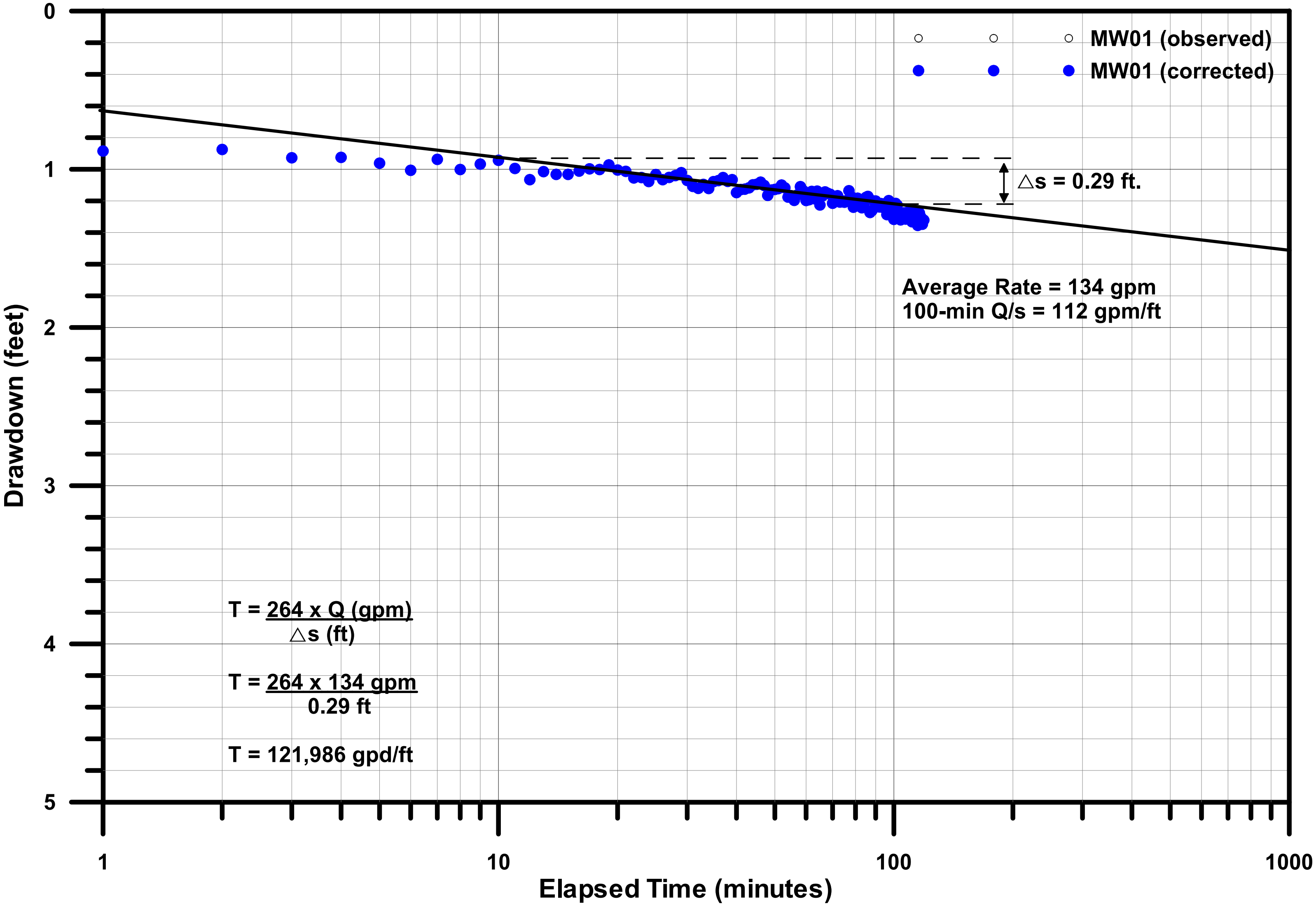
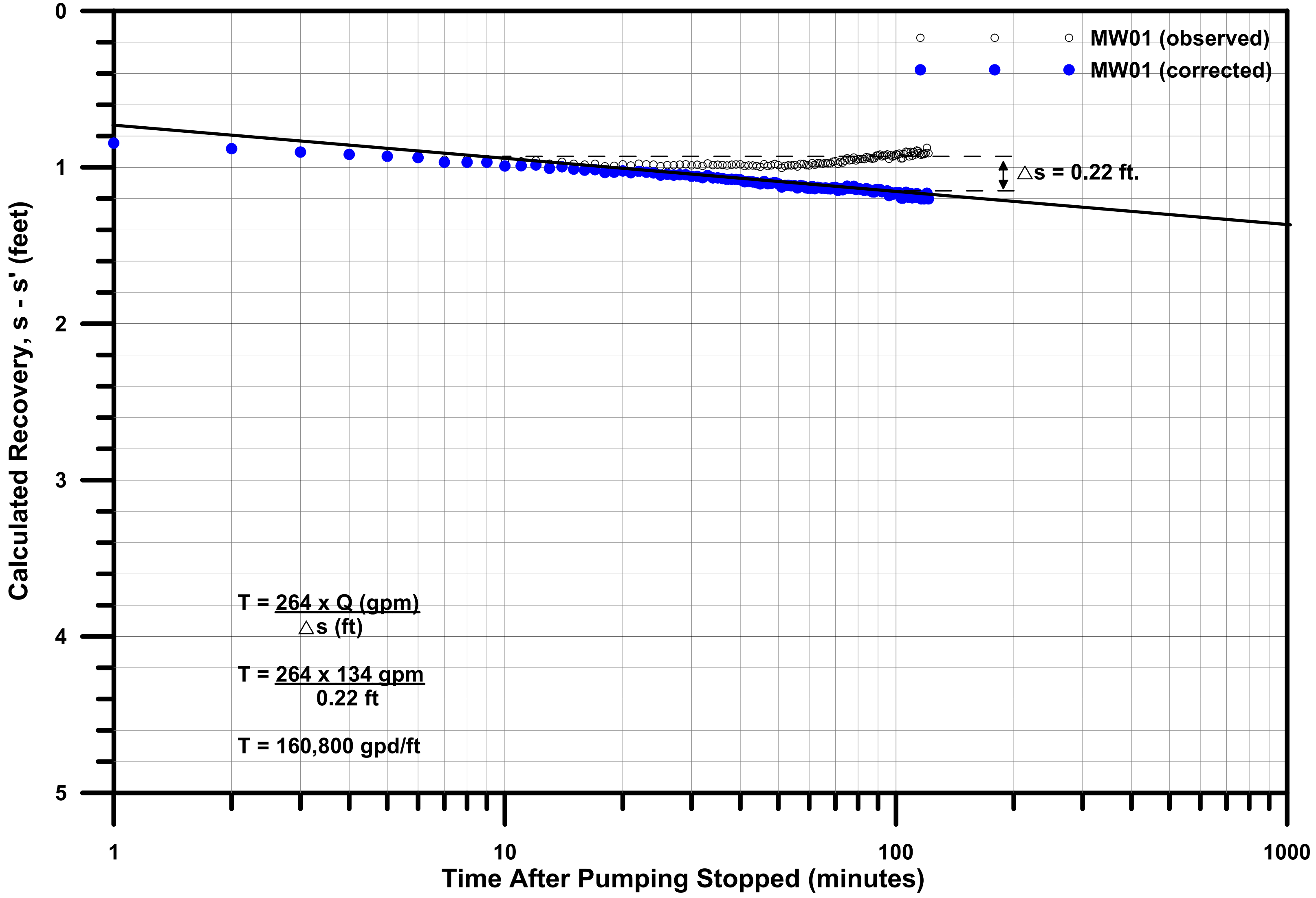
APPENDIX B – AQUIFER PARAMETER ANALYSES



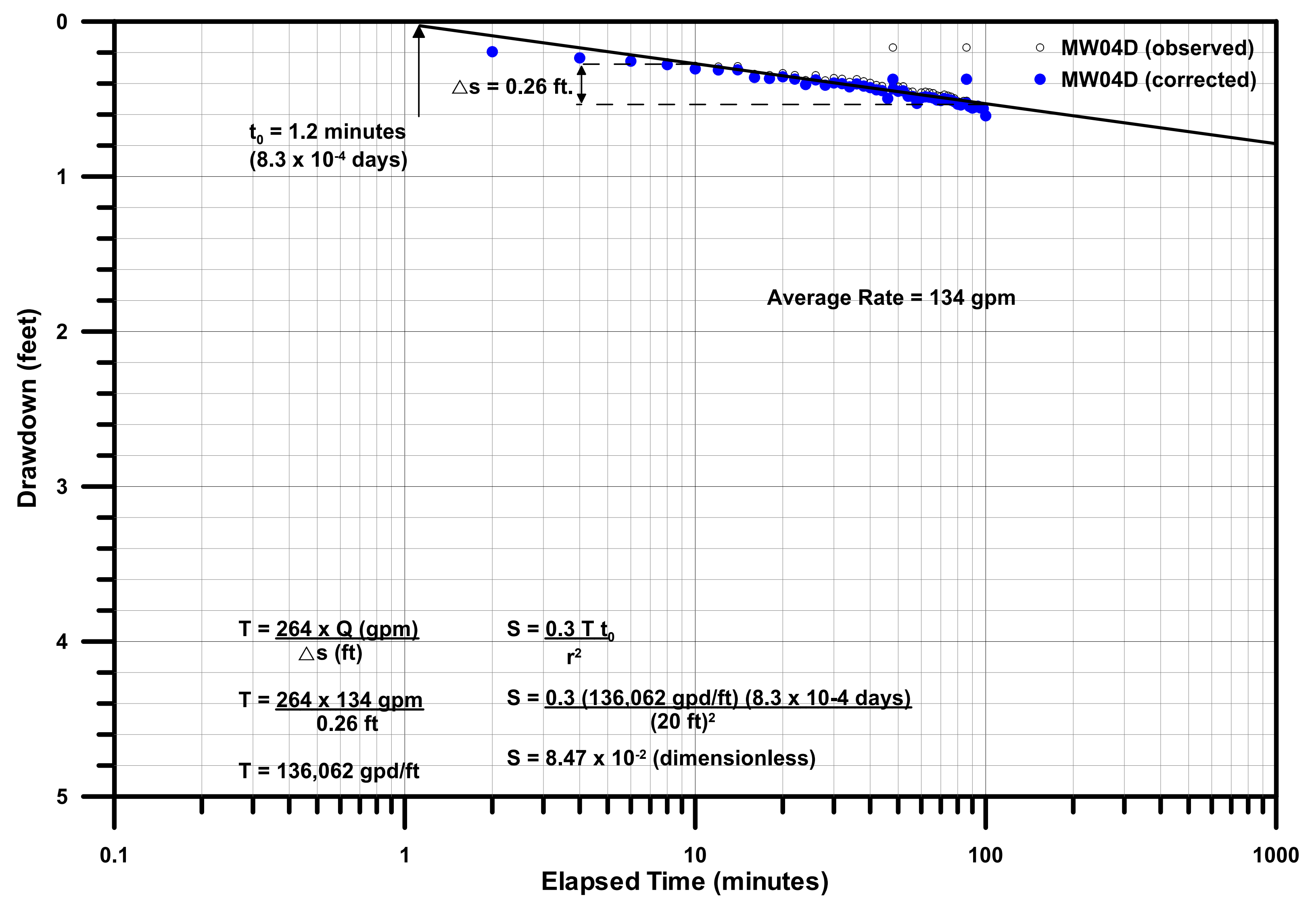
PUEBLO
water resources

FIGURE B1. MCWP-MW01 PRE-INJECTION PUMPING TEST - MW01 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B2. MCWP-MW01 PRE-INJECTION PUMPING TEST - MW01 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B3. MCWP-MW01 PRE-INJECTION PUMPING TEST - MW04D DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

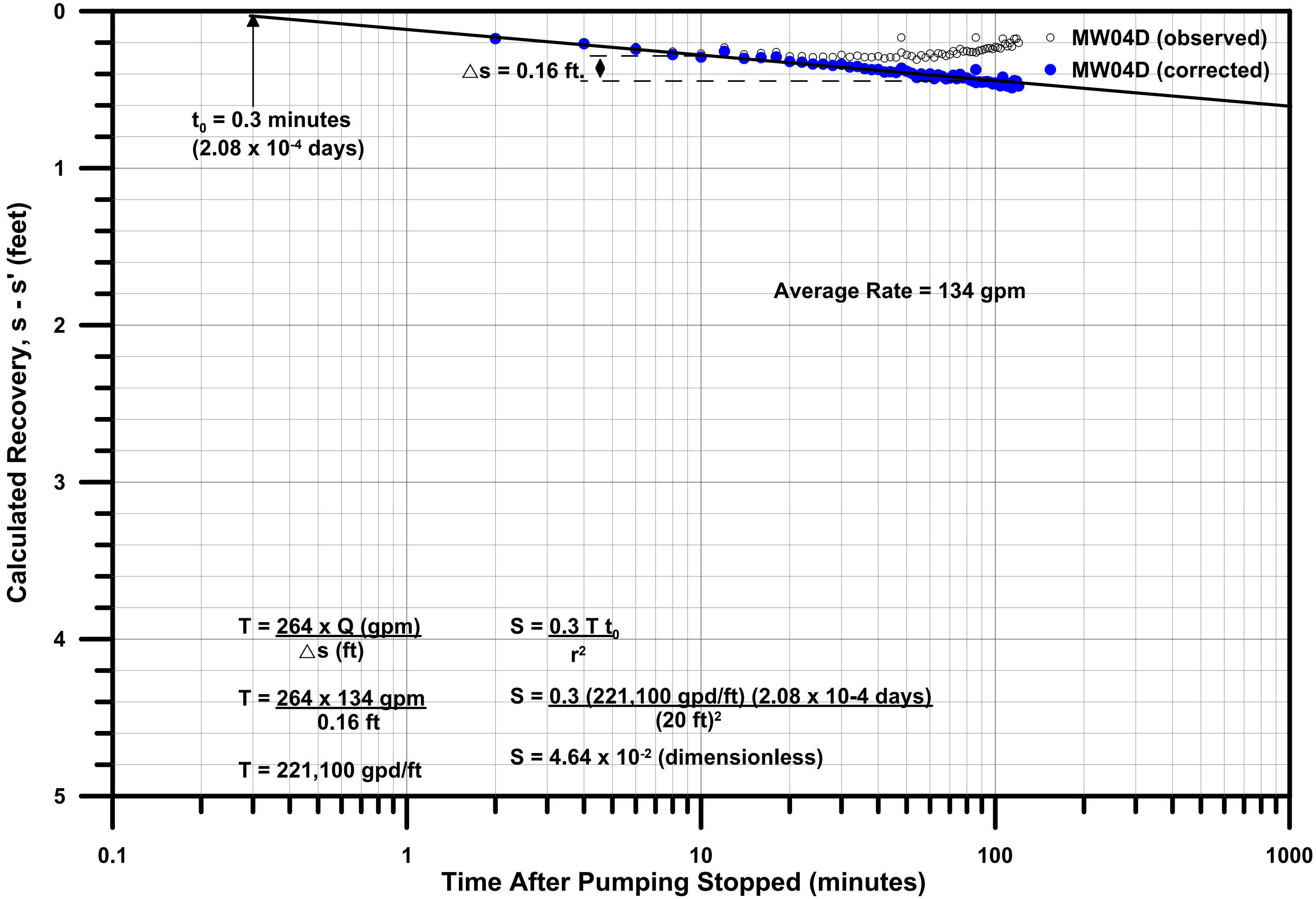
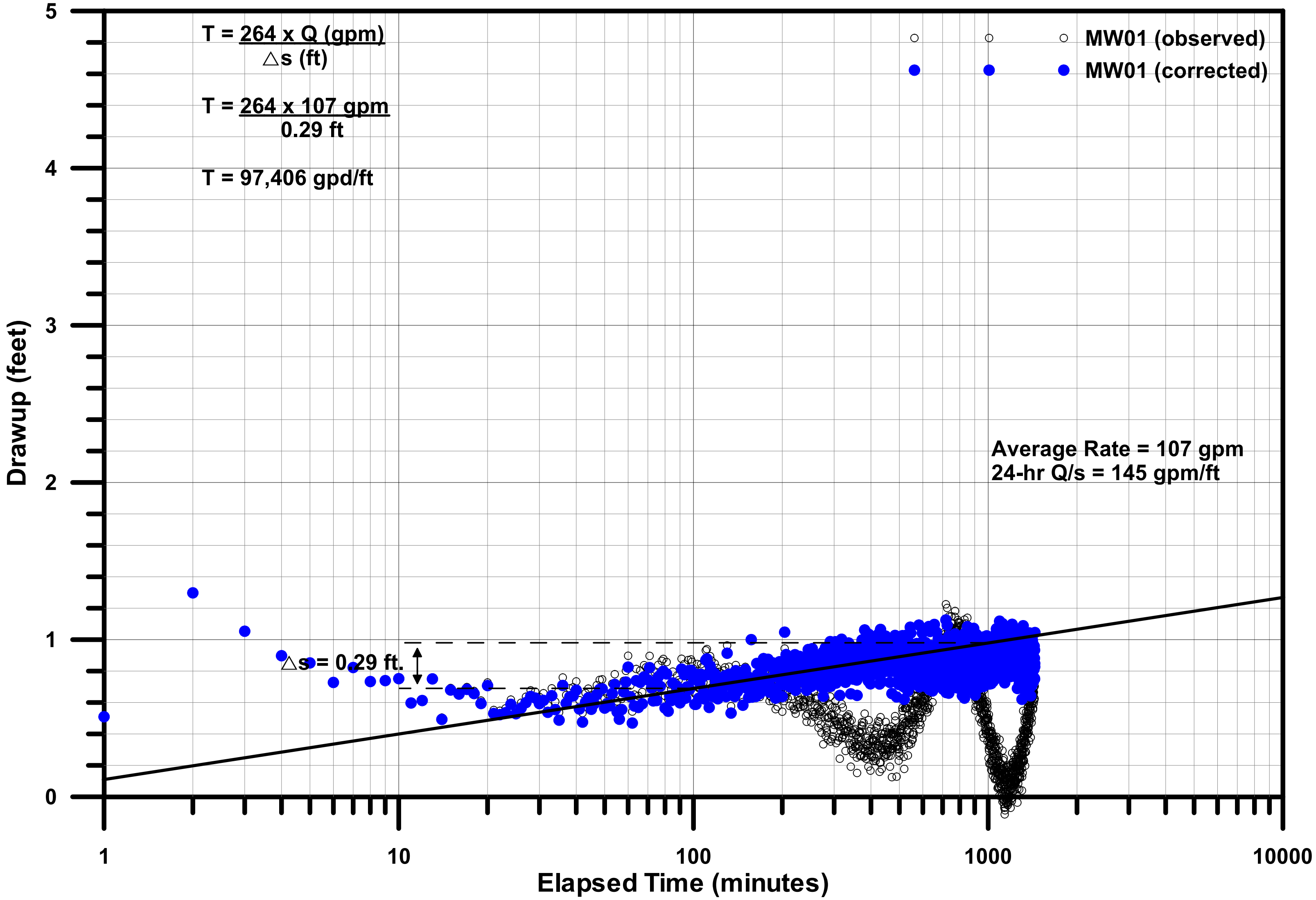
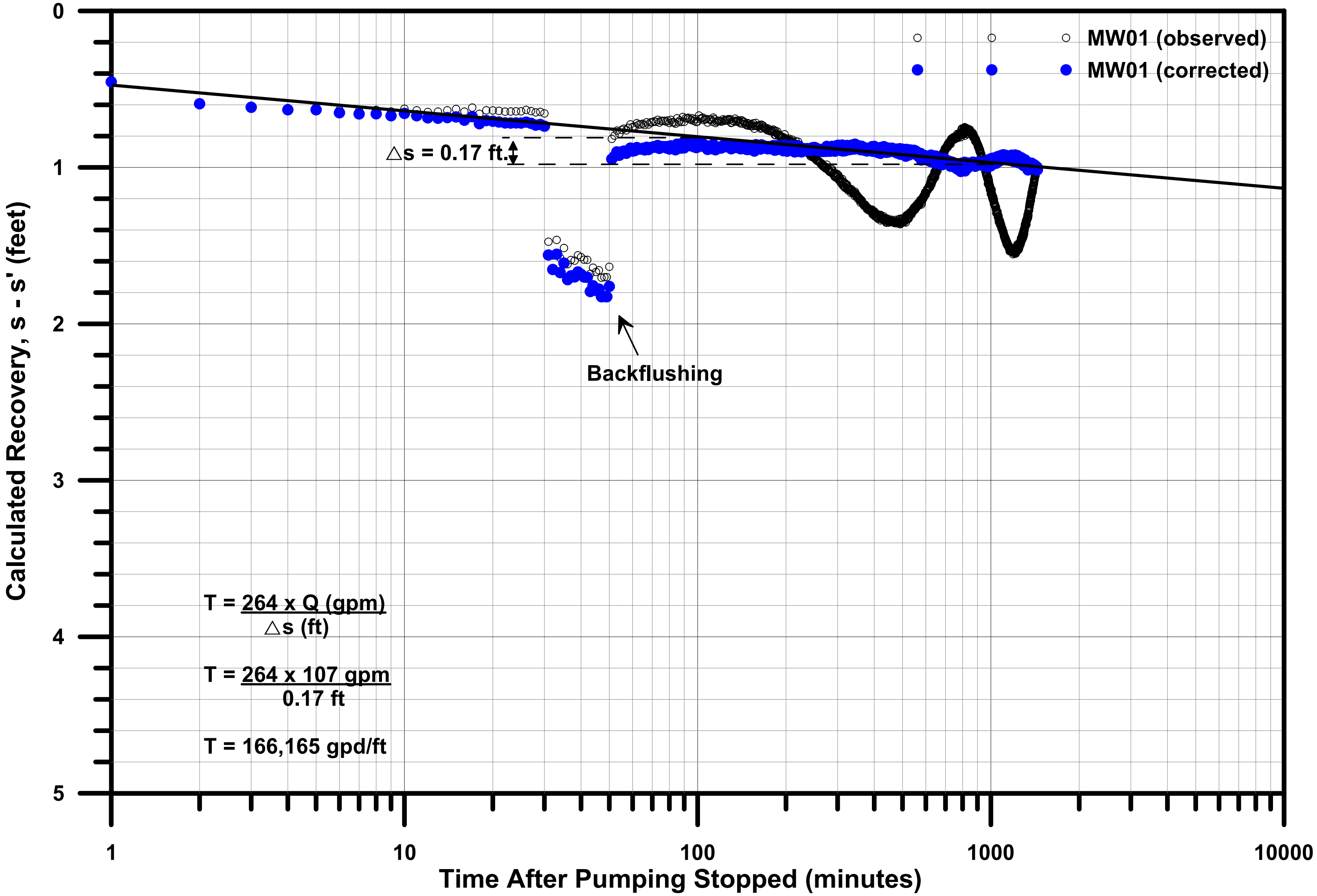


FIGURE B4. MCWP-MW01 PRE-INJECTION PUMPING TEST - MW04D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B5. MCWP-MW01 24-HR INJECTION TEST - MW01 DRAWUP DATA
Malibu Pilot Injection Testing Project
RMC Water and Environment / City of Malibu



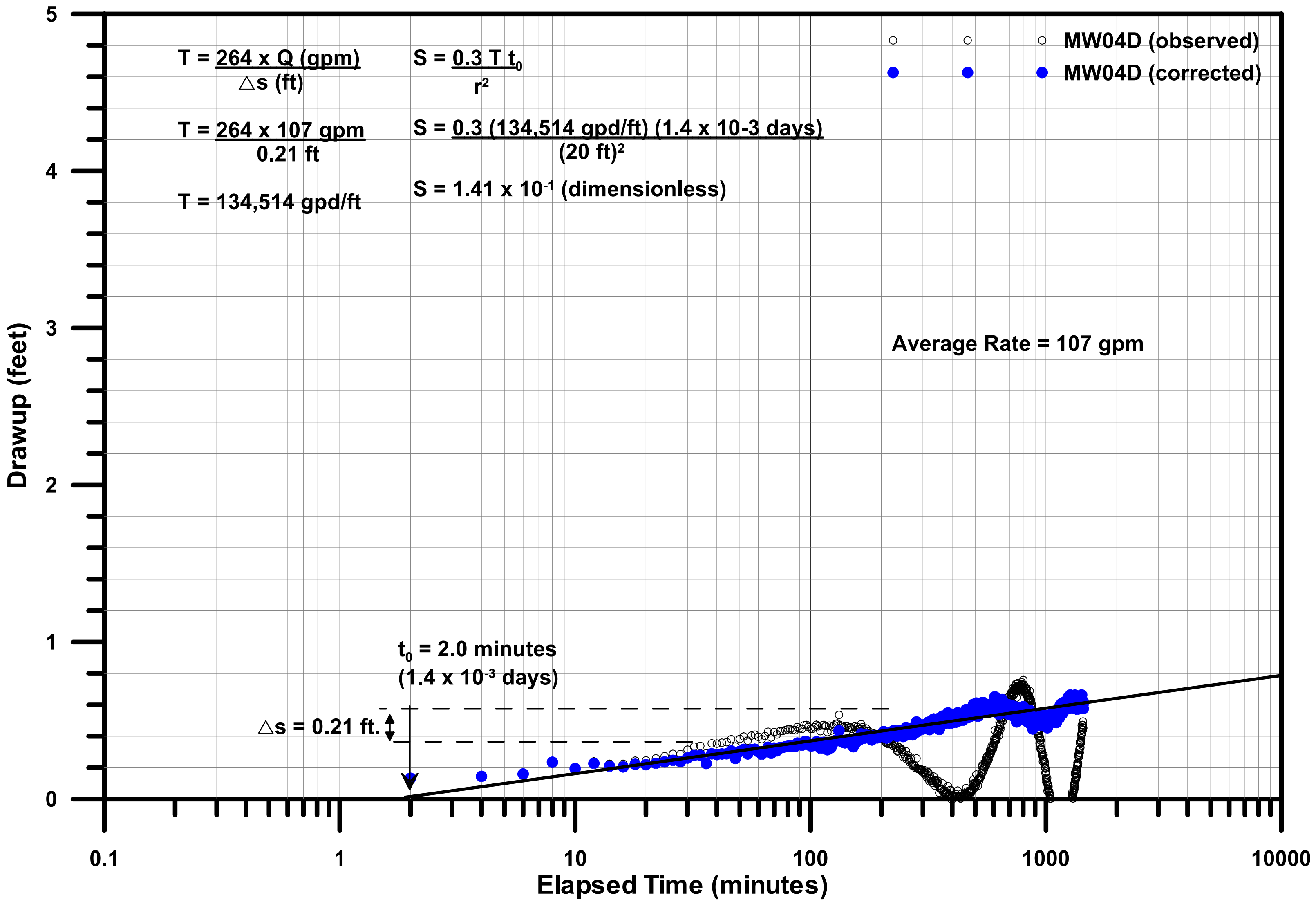
T = 264 x Q (gpm) / △s (ft)

T = 264 x 107 gpm / 0.17 ft

T = 166,165 gpd/ft

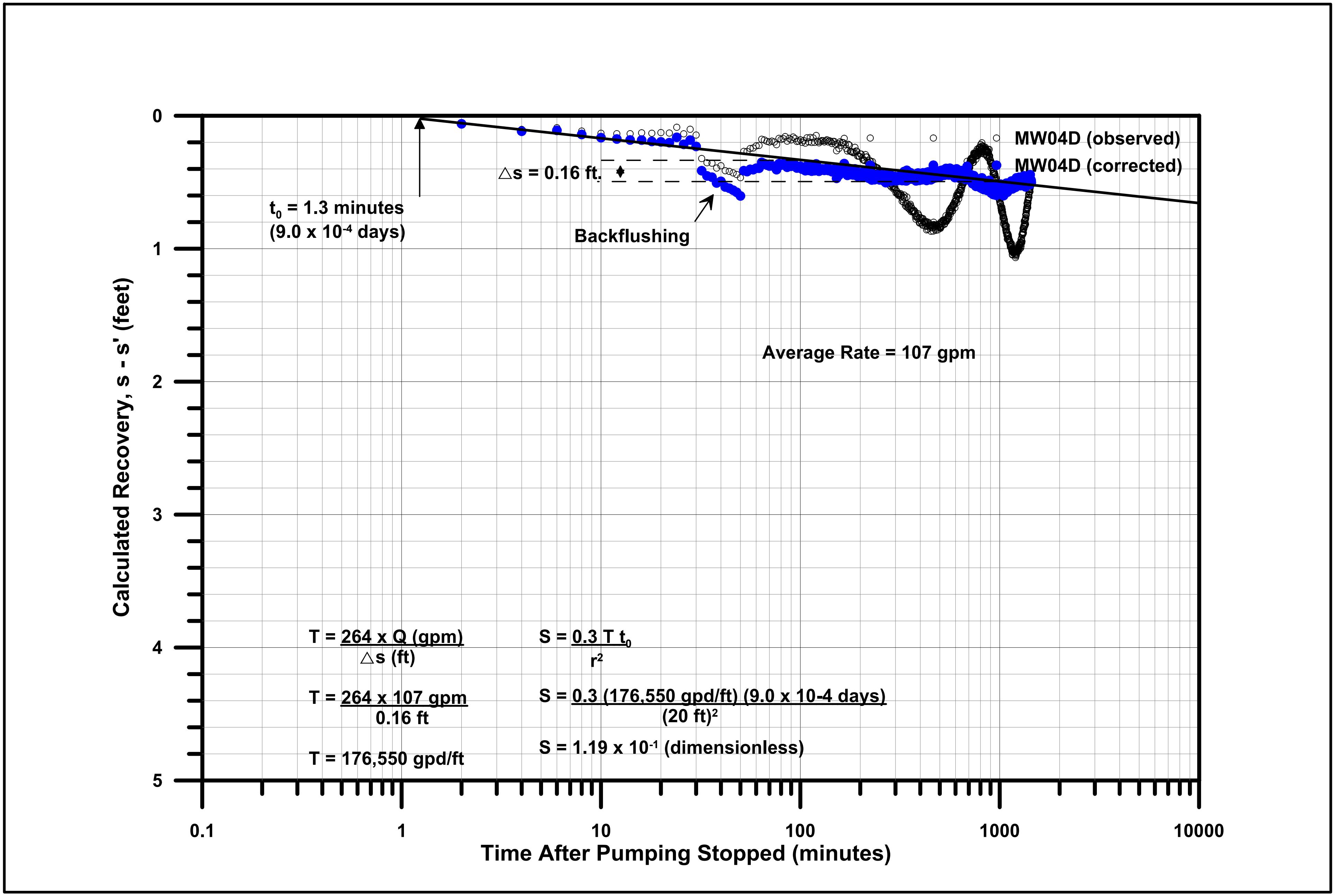
PUEBLO
water resources

FIGURE B6. MCWP-MW01 24-HR INJECTION TEST - MW01 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



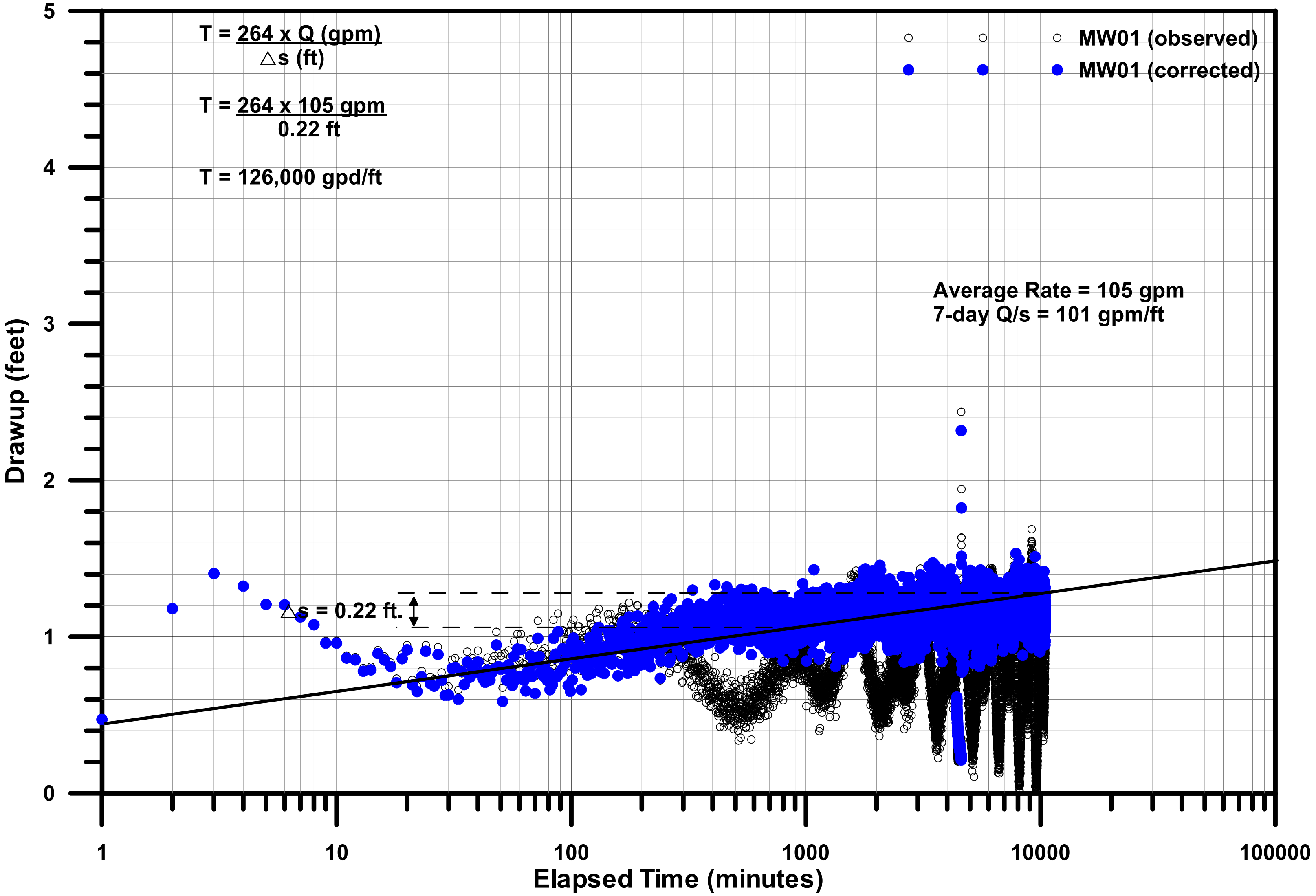
PUEBLO
water resources

FIGURE B7. MCWP-MW01 24-HR INJECTION TEST - MW04D DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



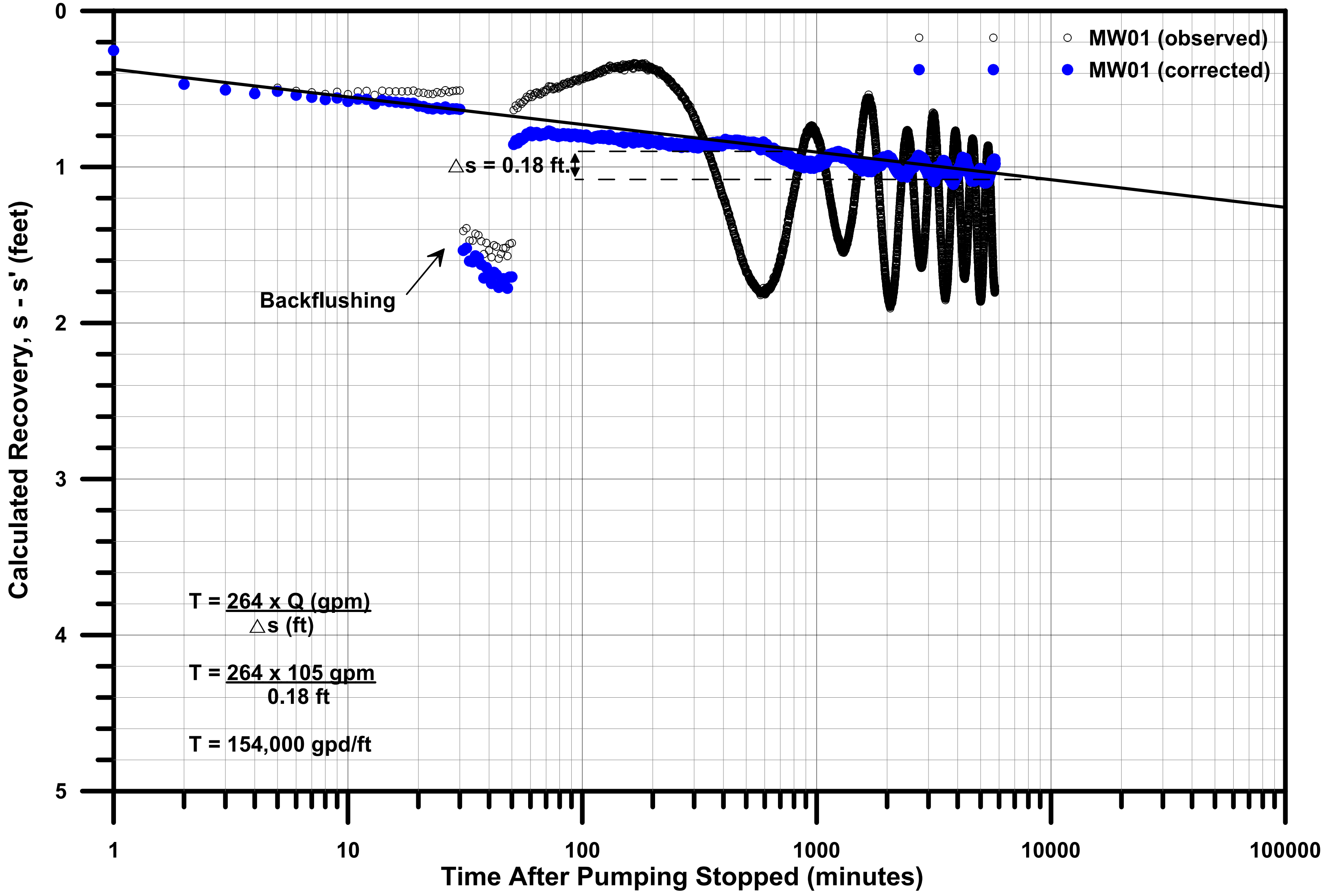
PUEBLO
water resources

FIGURE B8. MCWP-MW01 24-HR INJECTION TEST - MW04D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



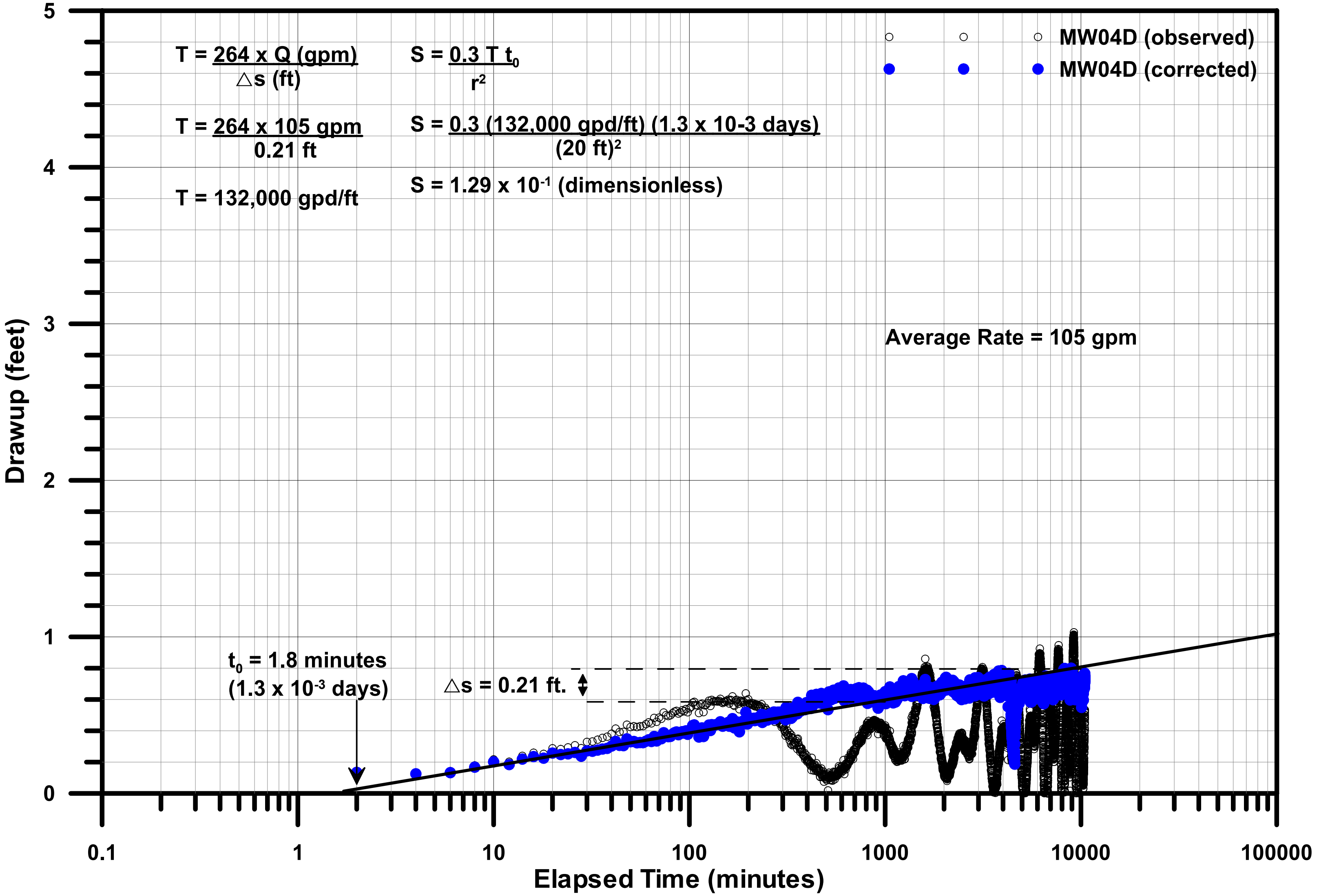
PUEBLO water resources

FIGURE B9. MCWP-MW01 7-DAY INJECTION TEST - MW01 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B10. MCWP-MW01 7-DAY INJECTION TEST - MW01 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



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water resources

FIGURE B11. MCWP-MW01 7-DAY INJECTION TEST - MW04D DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

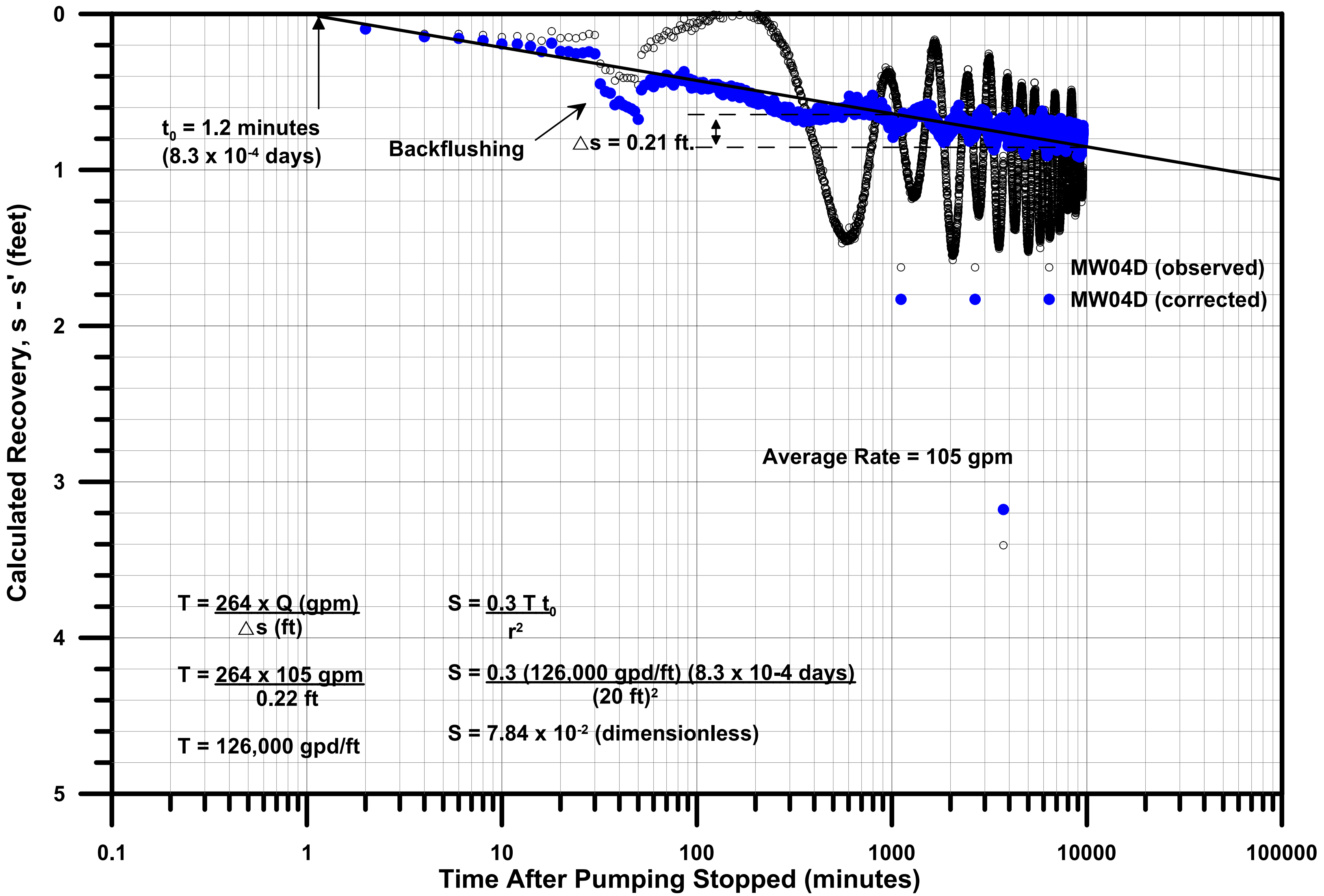
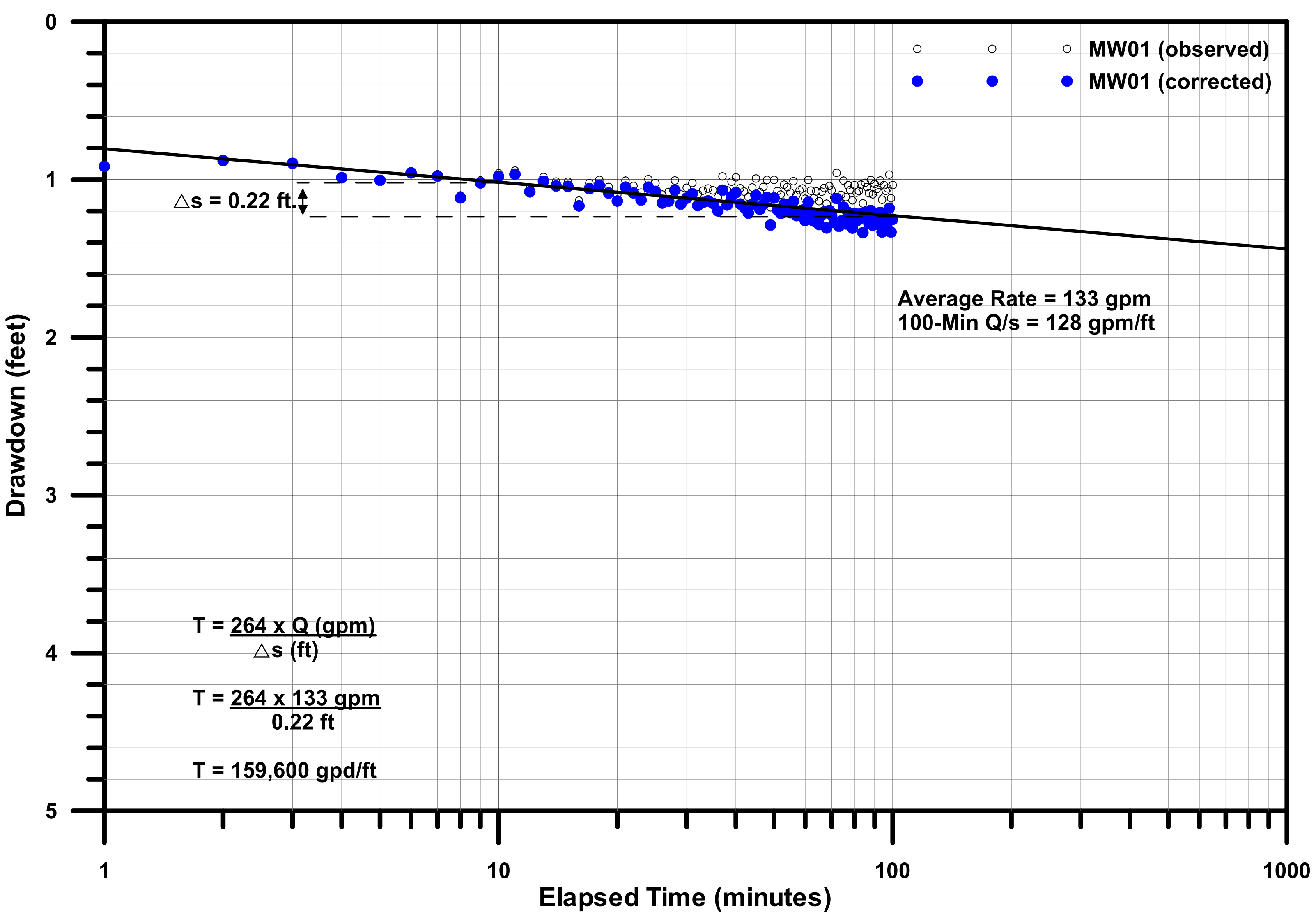


FIGURE B12. MCWP-MW01 7-DAY INJECTION TEST - MW04D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B13. MCWP-MW01 POST-INJECTION PUMPING TEST - MW01 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

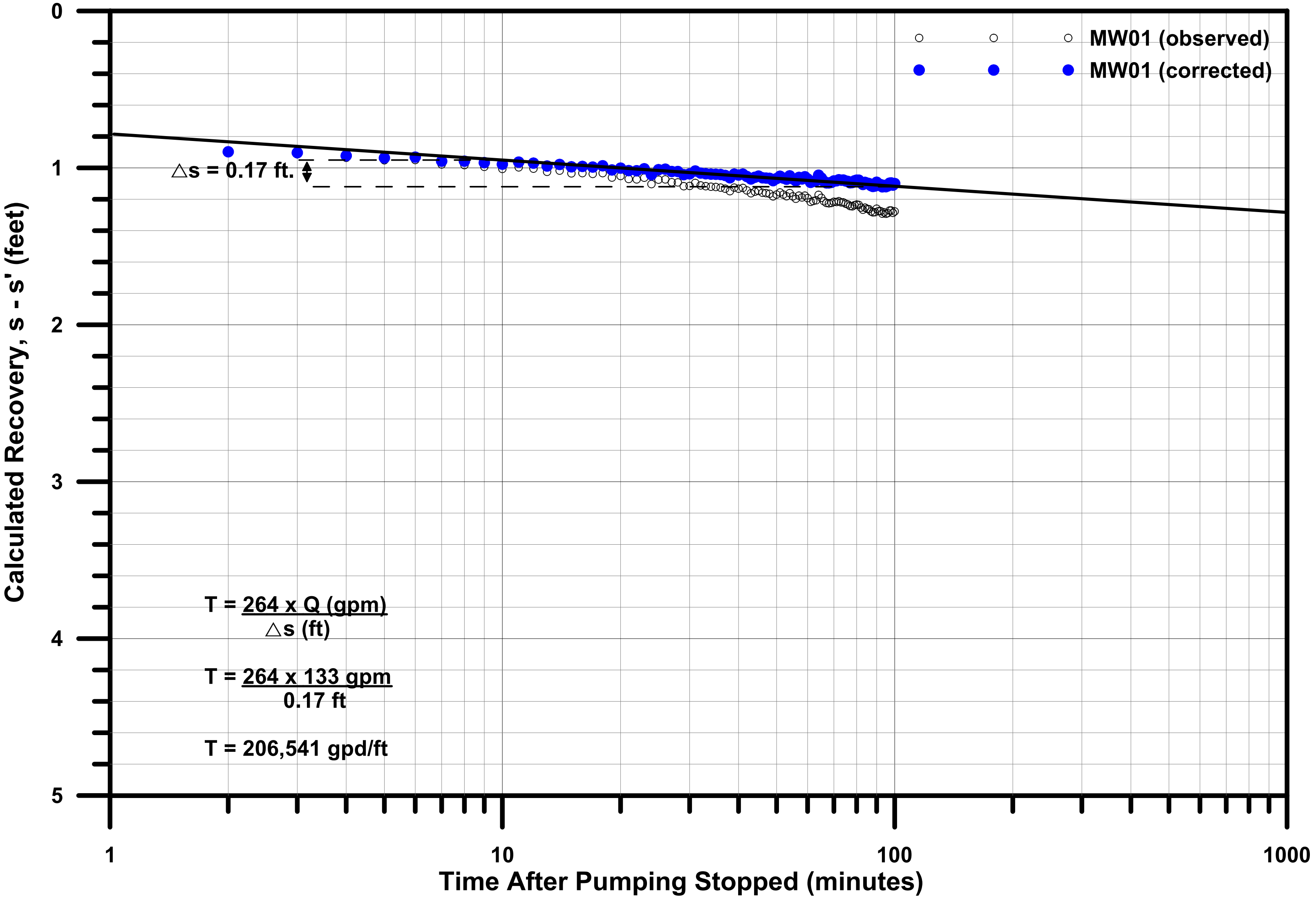


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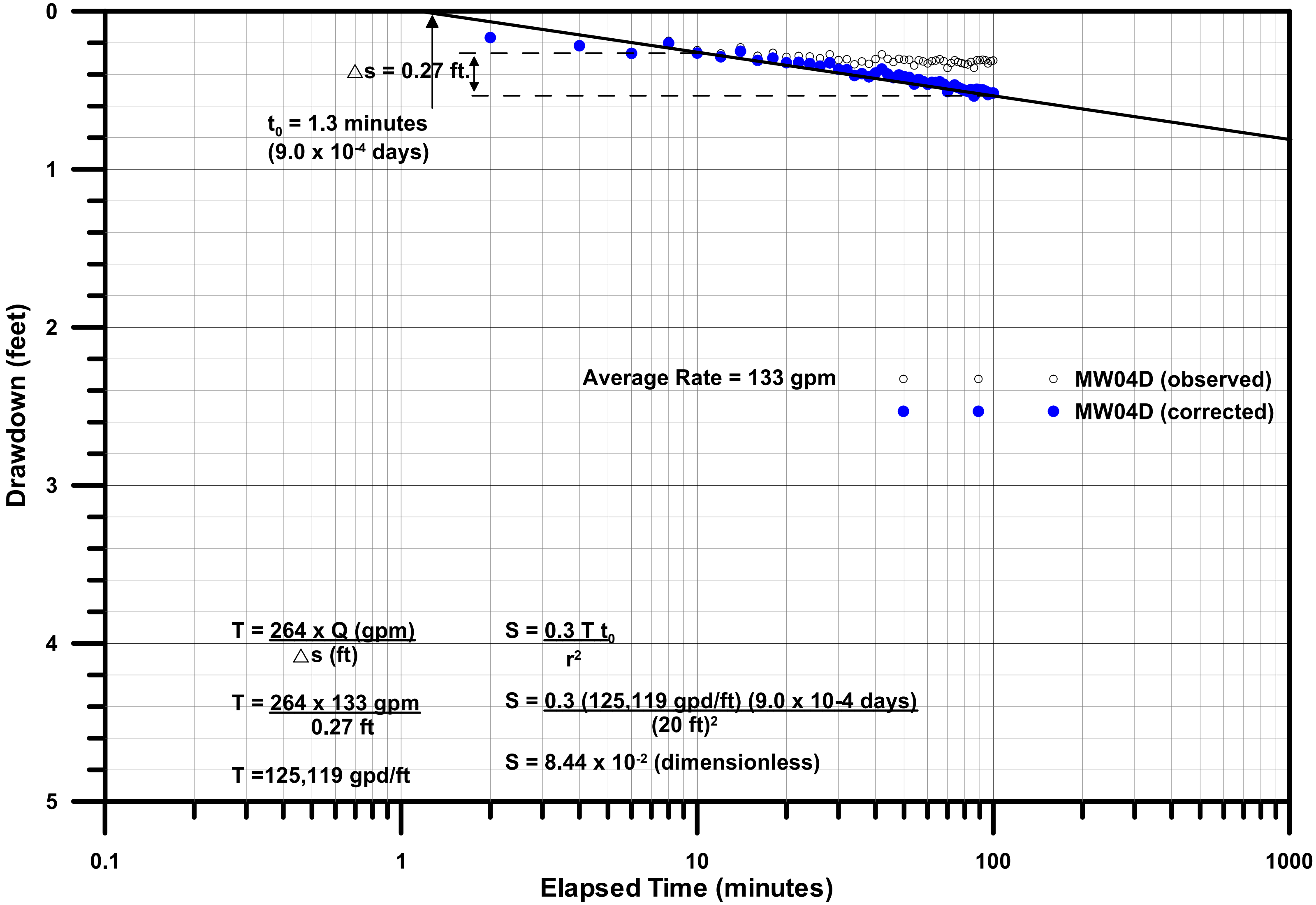
FIGURE B14. MCWP-MW01 POST-INJECTION PUMPING TEST - MW01 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{264 \times Q\ (\text{gpm})}{\triangle s\ (\text{ft})}$$

$$T = \frac{264 \times 133\ \text{gpm}}{0.27\ \text{ft}}$$

$$T = 125{,}119\ \text{gpd/ft}$$

$$S = \frac{0.3\ T\ t_0}{r^2}$$

$$S = \frac{0.3\ (125{,}119\ \text{gpd/ft})\ (9.0 \times 10\text{-}4\ \text{days})}{(20\ \text{ft})^2}$$

$$S = 8.44 \times 10^{-2}\ (\text{dimensionless})$$

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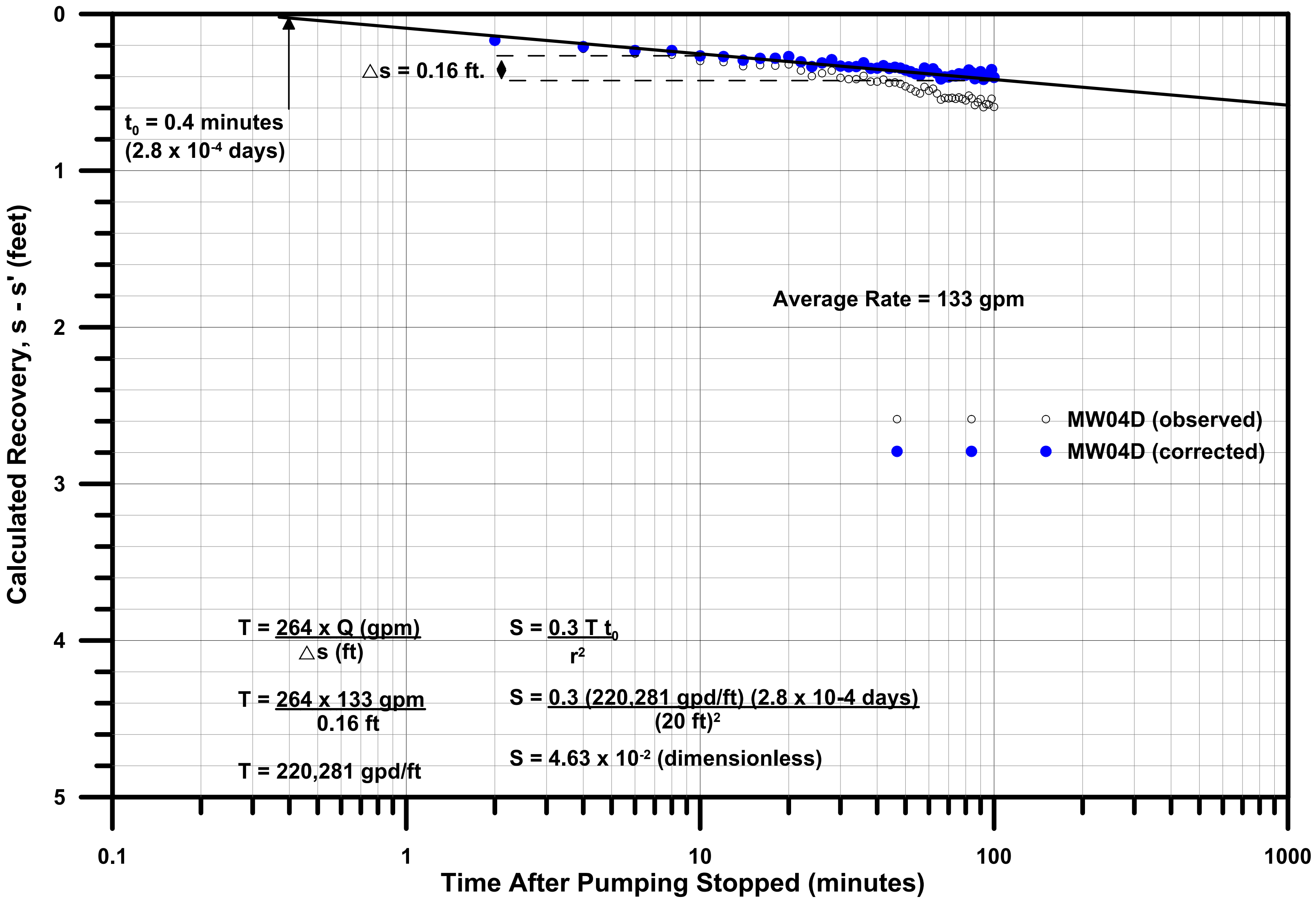
water resources

FIGURE B15. MCWP-MW01 POST-INJECTION PUMPING TEST - MW04D DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$T = \dfrac{264 \times Q \text{ (gpm)}}{\triangle s \text{ (ft)}}$

$T = \dfrac{264 \times 133 \text{ gpm}}{0.16 \text{ ft}}$

T = 220,281 gpd/ft

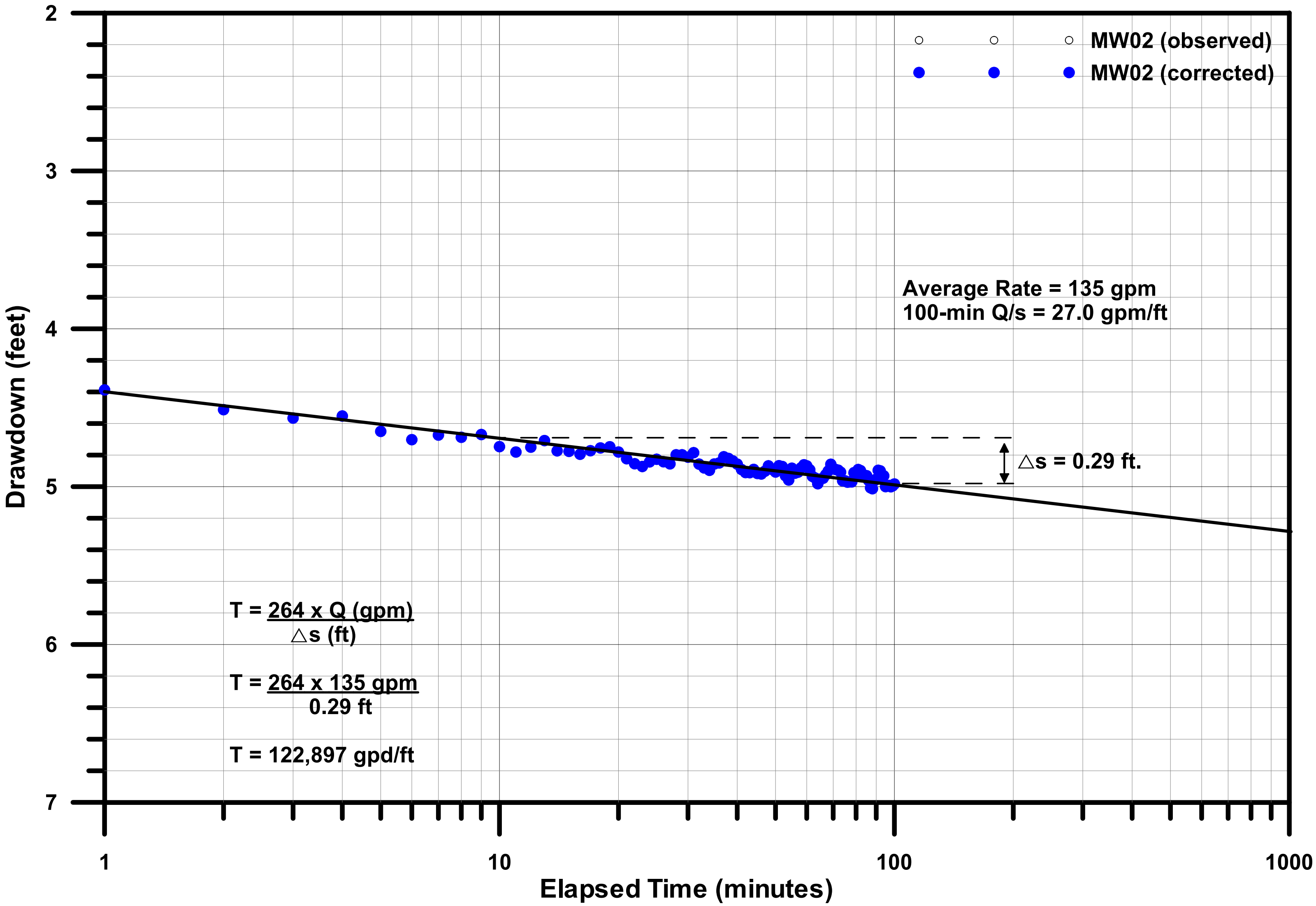
$S = \dfrac{0.3\ T\ t_0}{r^2}$

$S = \dfrac{0.3 \text{ (220,281 gpd/ft) (2.8 x 10-4 days)}}{(20 \text{ ft})^2}$

$S = 4.63 \times 10^{-2}$ (dimensionless)

PUEBLO
water resources

FIGURE B16. MCWP-MW01 POST-INJECTION PUMPING TEST - MW04D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B17. MCWP-MW02 PRE-INJECTION PUMPING TEST - MW02 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

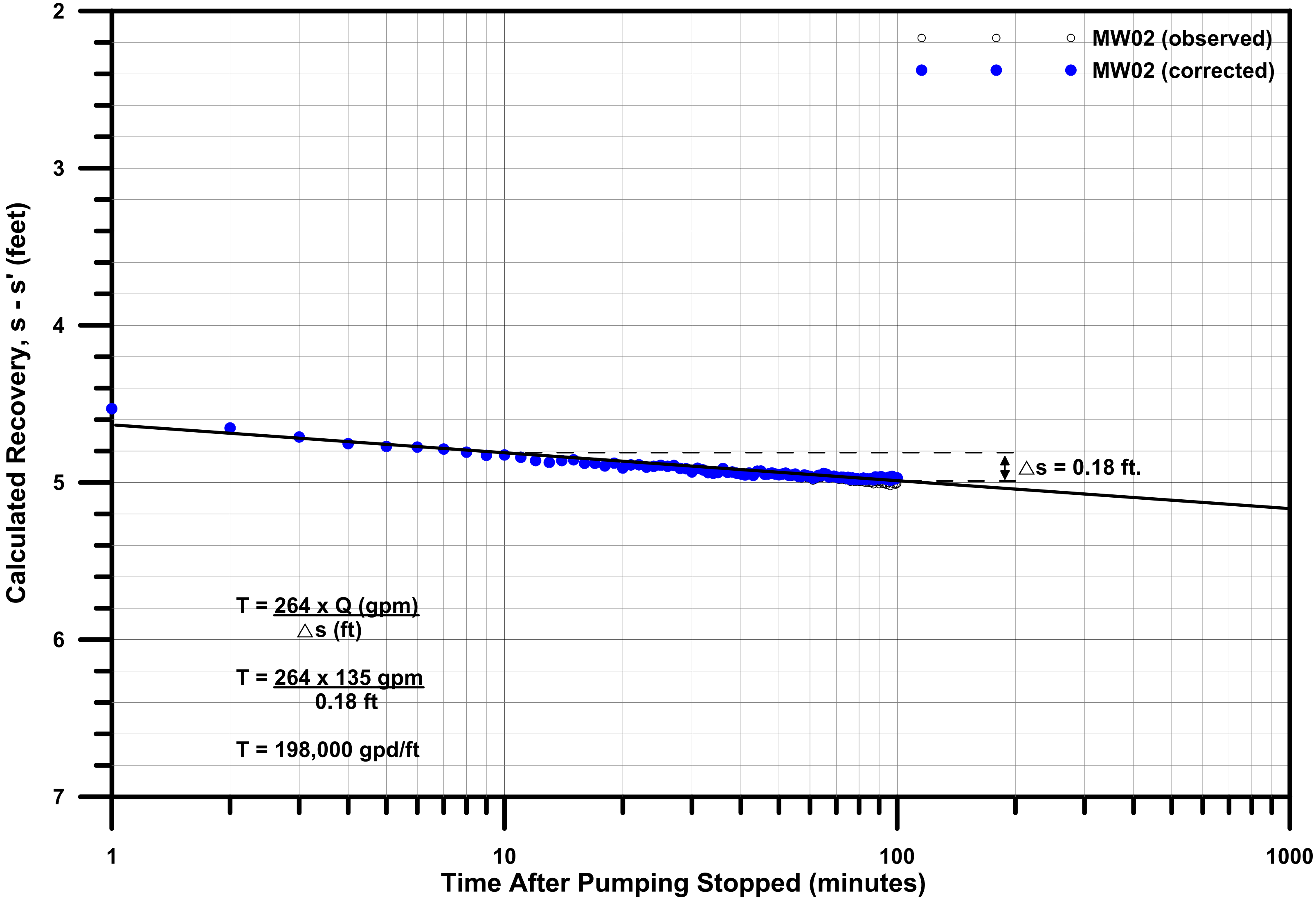
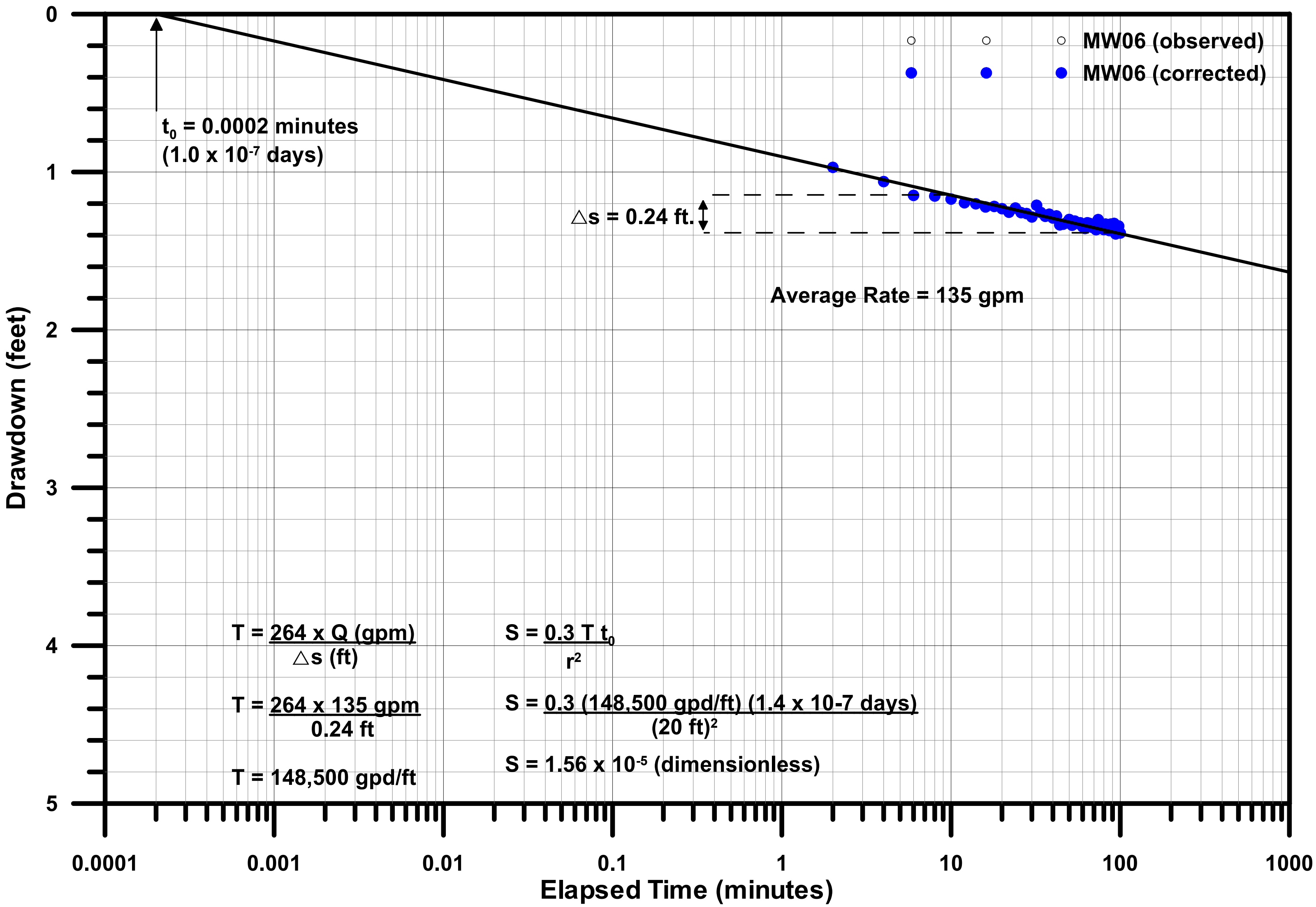


FIGURE B18. MCWP-MW02 PRE-INJECTION PUMPING TEST - MW02 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{264 \times Q\ (\text{gpm})}{\triangle s\ (\text{ft})}$$

$$T = \frac{264 \times 135\ \text{gpm}}{0.24\ \text{ft}}$$

T = 148,500 gpd/ft

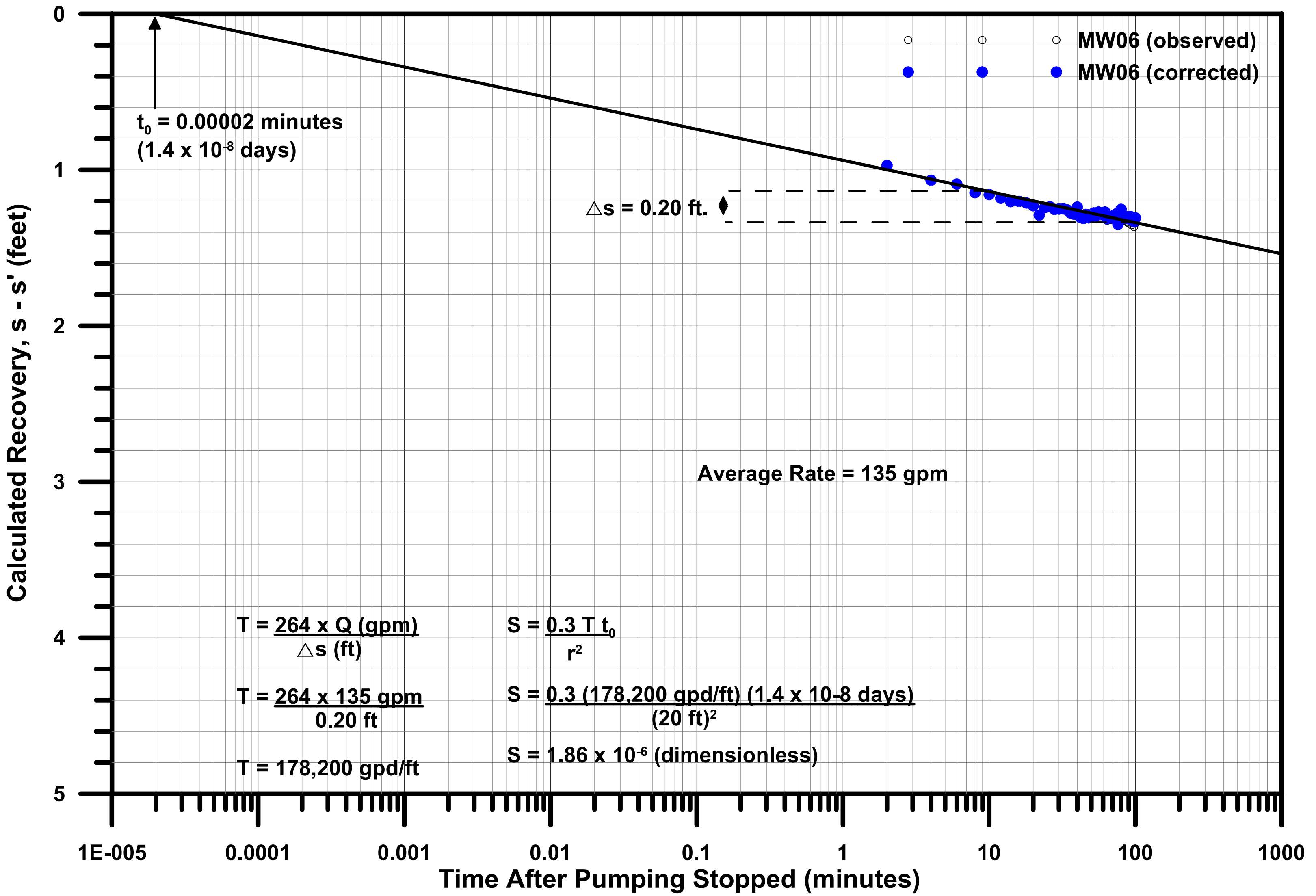
$$S = \frac{0.3\ T\ t_0}{r^2}$$

$$S = \frac{0.3\ (148{,}500\ \text{gpd/ft})\ (1.4 \times 10\text{-}7\ \text{days})}{(20\ \text{ft})^2}$$

S = 1.56 x 10^{-5} (dimensionless)

PUEBLO water resources

FIGURE B19. MCWP-MW02 PRE-INJECTION PUMPING TEST - MW06 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{264 \times Q\ (\text{gpm})}{\triangle s\ (\text{ft})}$$

$$T = \frac{264 \times 135\ \text{gpm}}{0.20\ \text{ft}}$$

T = 178,200 gpd/ft

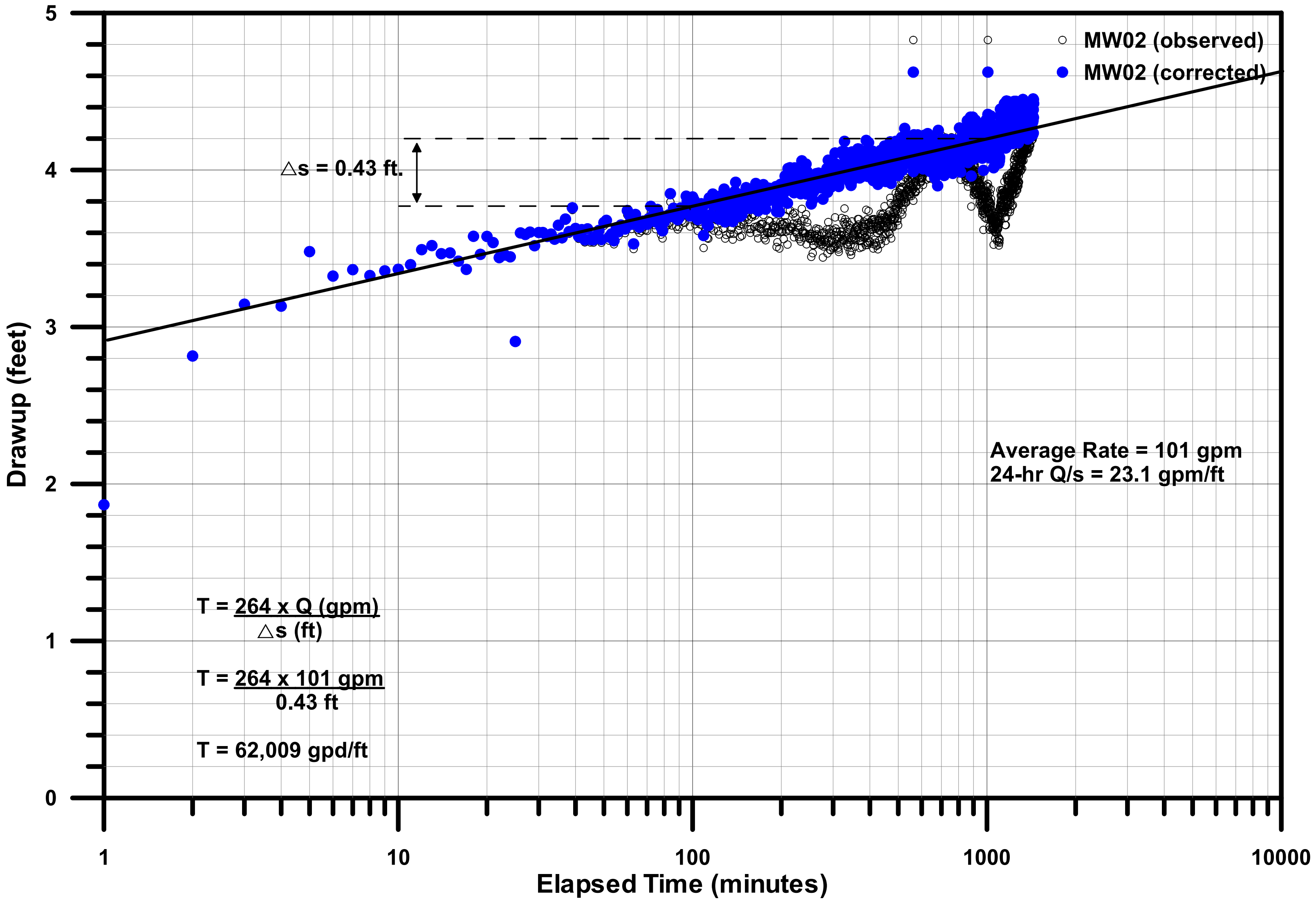
$$S = \frac{0.3\ T\ t_0}{r^2}$$

$$S = \frac{0.3\ (178{,}200\ \text{gpd/ft})\ (1.4 \times 10\text{-}8\ \text{days})}{(20\ \text{ft})^2}$$

S = 1.86 x 10^{-6} (dimensionless)

PUEBLO
water resources

FIGURE B20. MCWP-MW02 PRE-INJECTION PUMPING TEST - MW06 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



Average Rate = 101 gpm
24-hr Q/s = 23.1 gpm/ft

$$T = \frac{264 \times Q\ (\text{gpm})}{\triangle s\ (\text{ft})}$$

$$T = \frac{264 \times 101\ \text{gpm}}{0.43\ \text{ft}}$$

T = 62,009 gpd/ft

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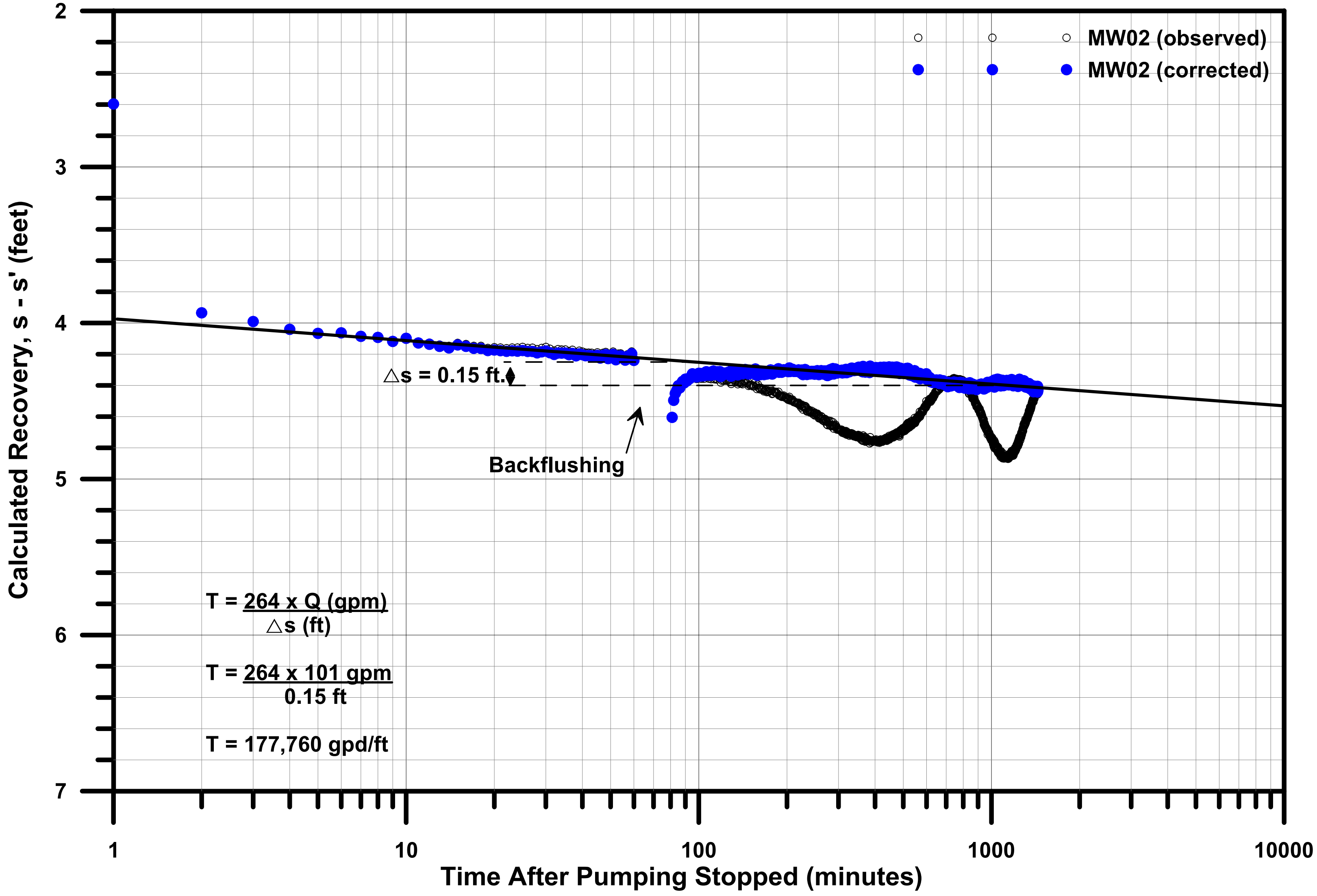
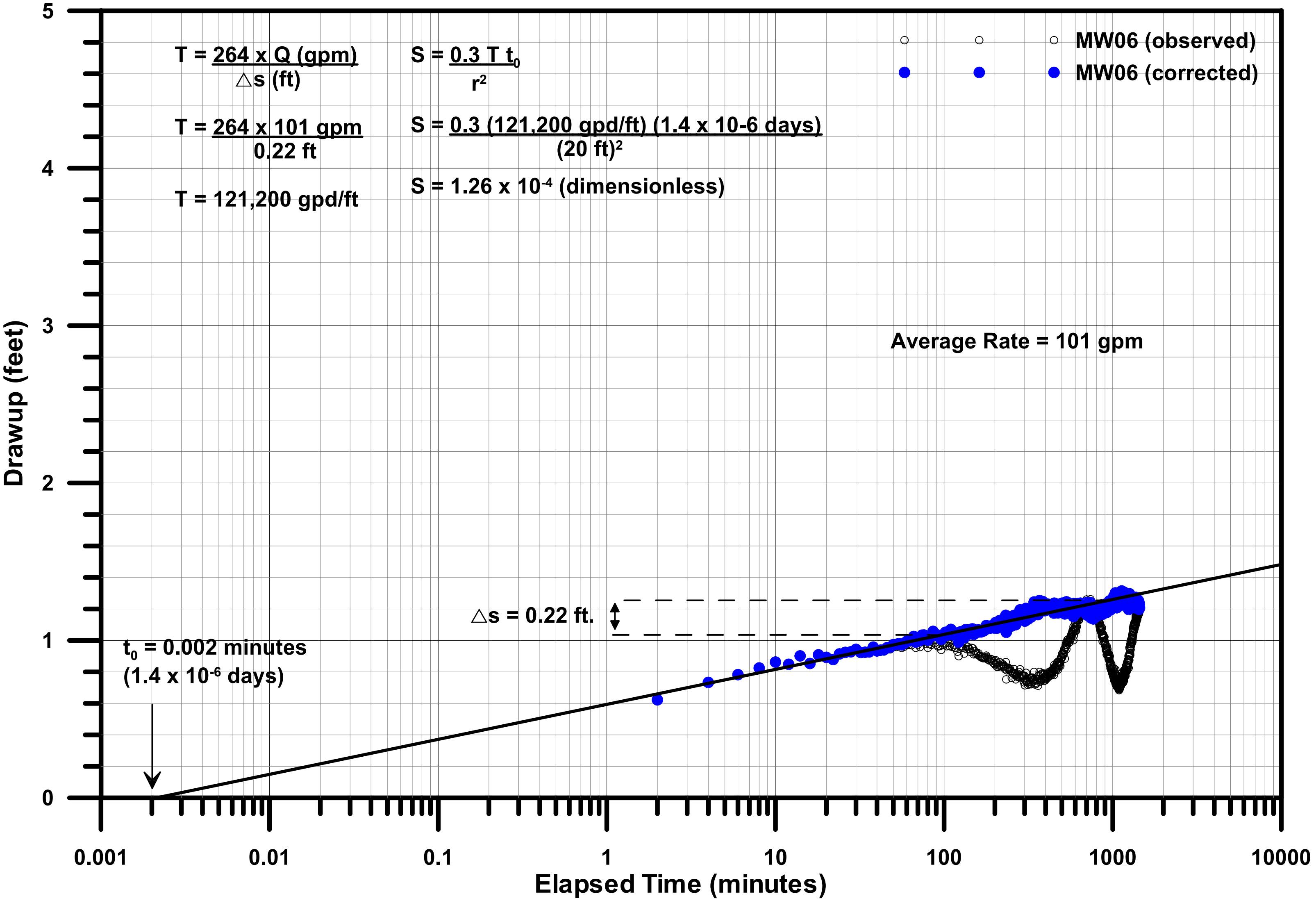
water resources

FIGURE B21. MCWP-MW02 24-HR INJECTION TEST - MW02 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



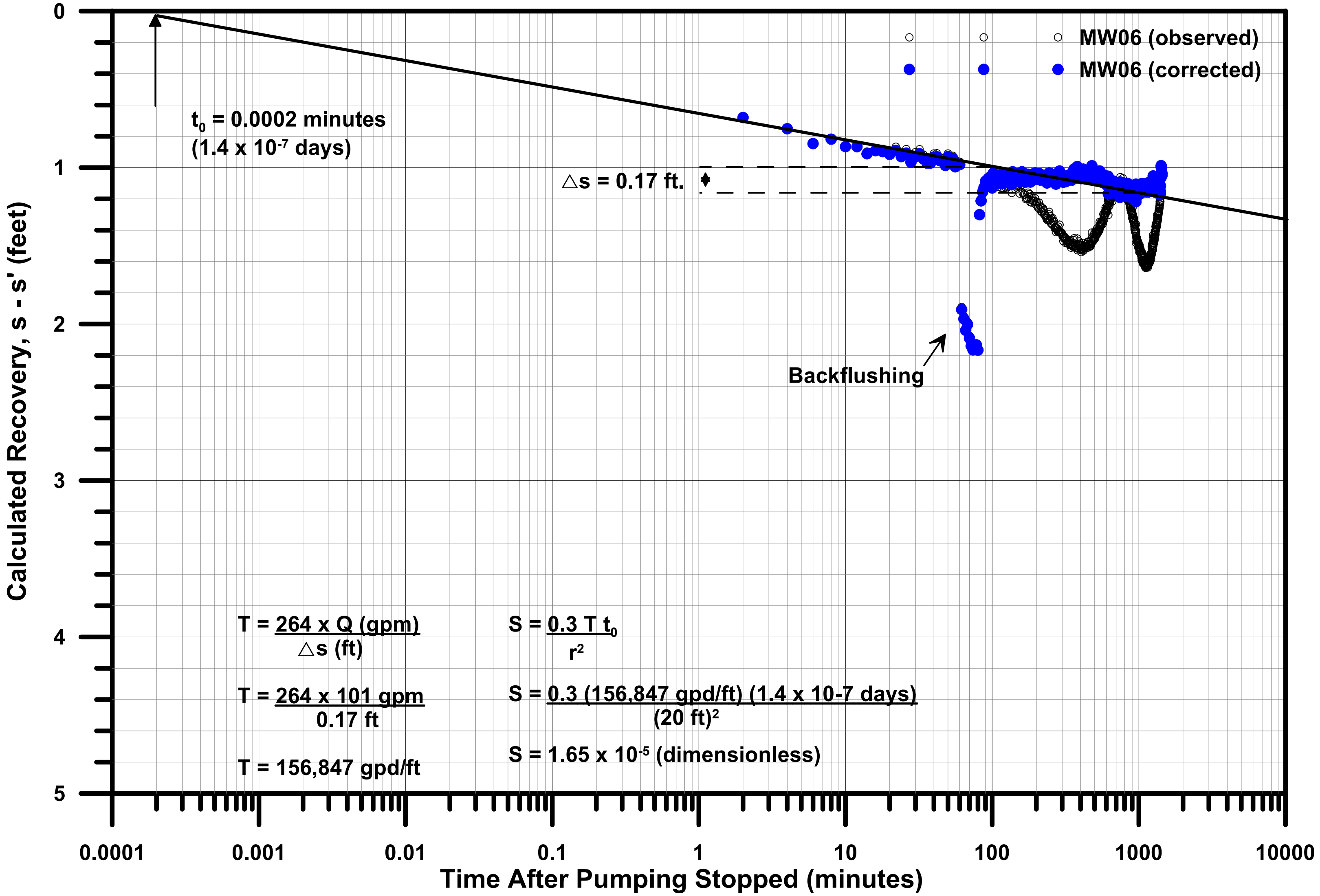
PUEBLO water resources

FIGURE B22. MCWP-MW02 24-HR INJECTION TEST - MW02 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B23. MCWP-MW02 24-HR INJECTION TEST - MW06 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{264 \text{ x } Q \text{ (gpm)}}{\triangle s \text{ (ft)}}$$

$$T = \frac{264 \text{ x } 101 \text{ gpm}}{0.17 \text{ ft}}$$

$$T = 156{,}847 \text{ gpd/ft}$$

$$S = \frac{0.3\ T\ t_0}{r^2}$$

$$S = \frac{0.3\ (156{,}847 \text{ gpd/ft})\ (1.4 \text{ x } 10\text{-}7 \text{ days})}{(20 \text{ ft})^2}$$

$$S = 1.65 \text{ x } 10^{-5} \text{ (dimensionless)}$$

PUEBLO
water resources

FIGURE B24. MCWP-MW02 24-HR INJECTION TEST - MW06 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

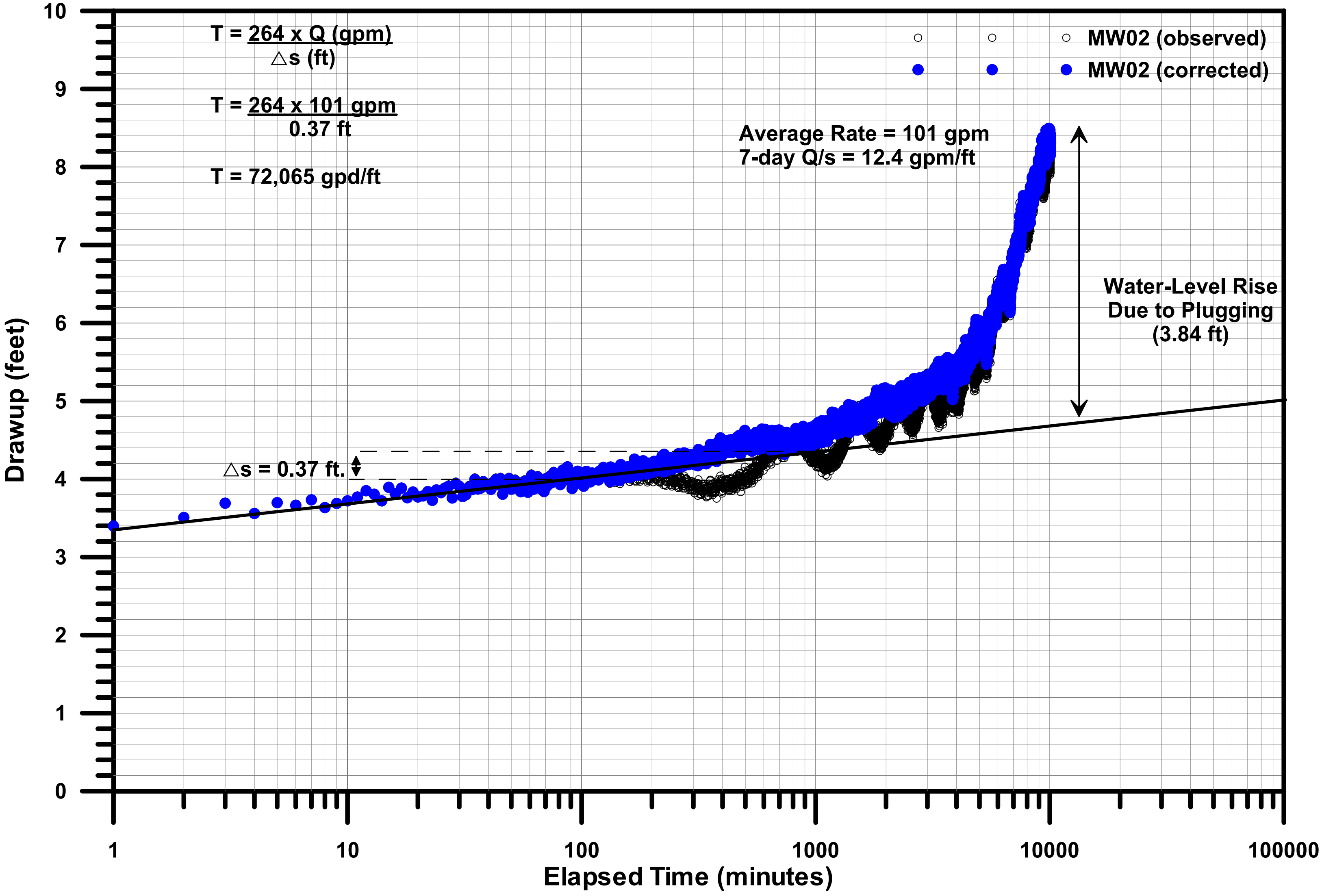
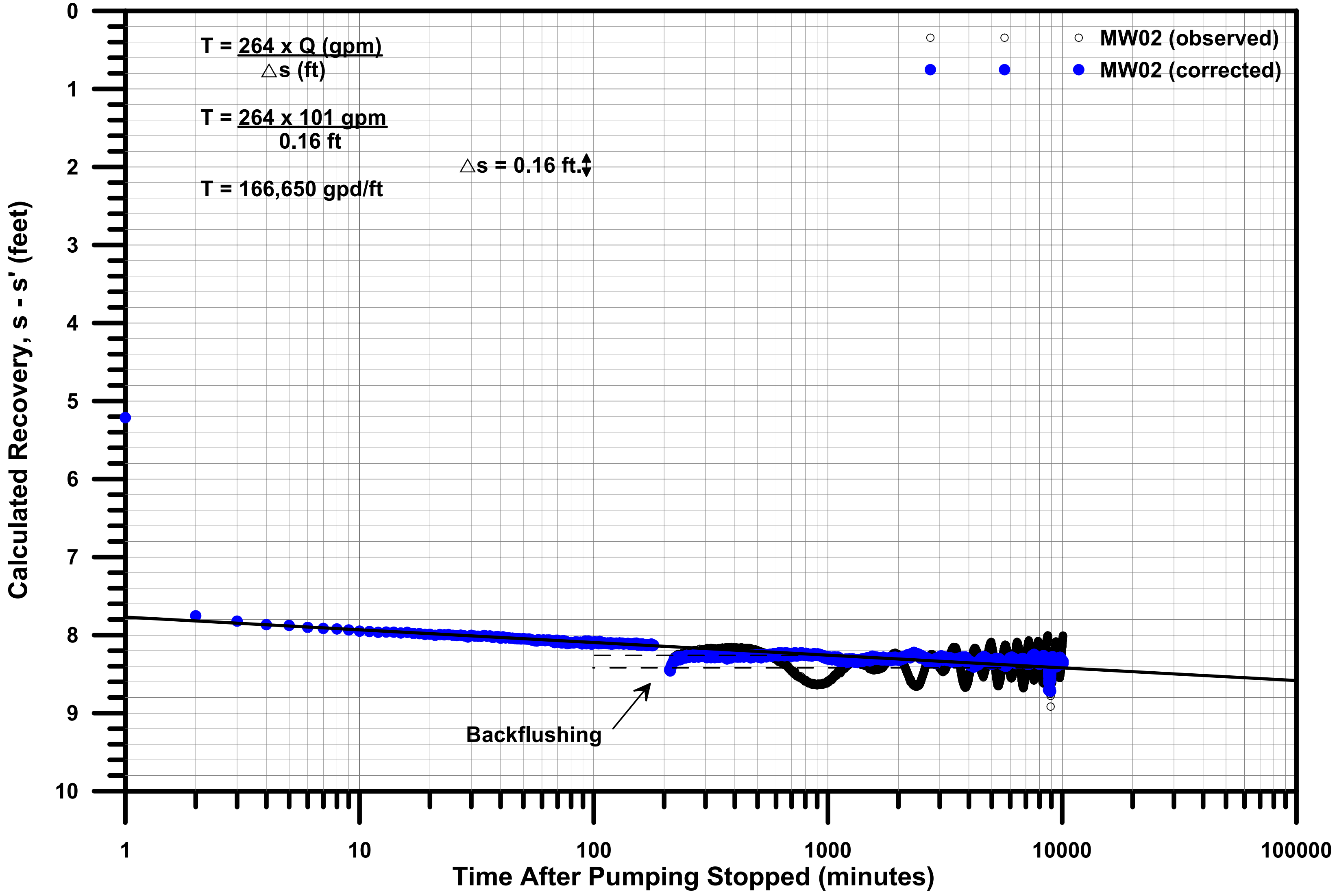


FIGURE B25. MCWP-MW02 7-DAY INJECTION TEST - MW02 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



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water resources

FIGURE B26. MCWP-MW02 7-DAY INJECTION TEST - MW02 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

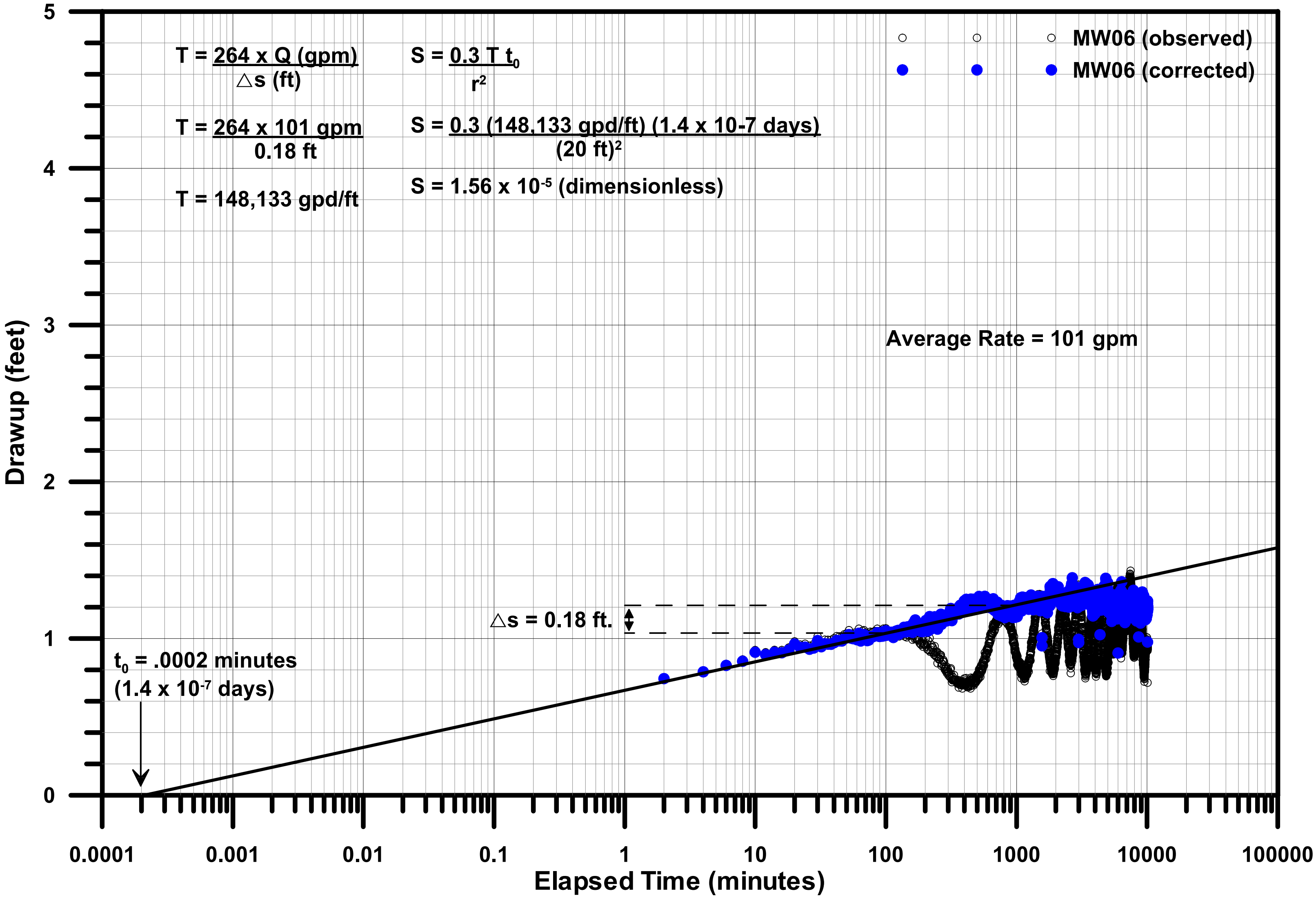
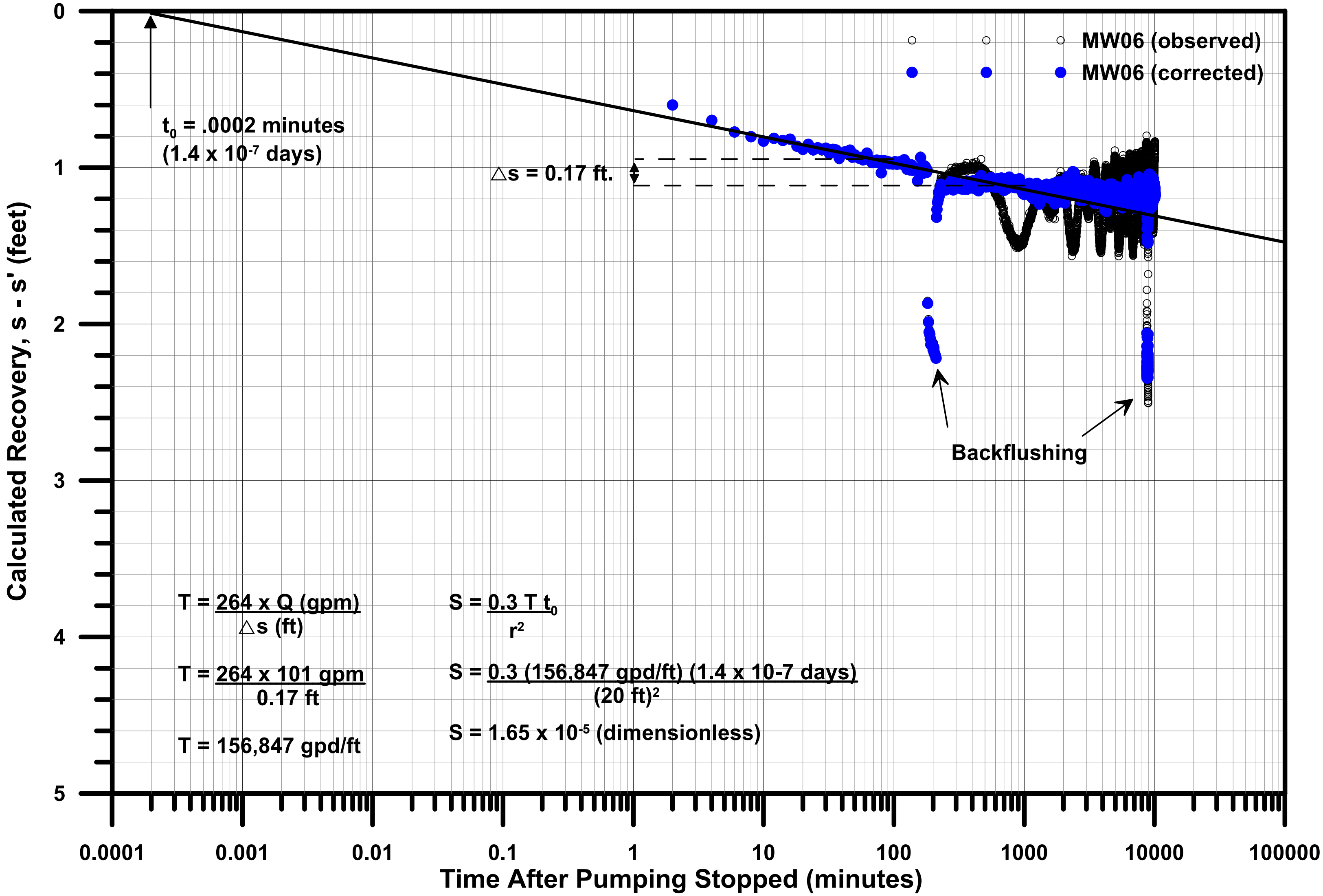


FIGURE B27. MCWP-MW02 7-DAY INJECTION TEST - MW06 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B28. MCWP-MW02 7-DAY INJECTION TEST - MW06 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

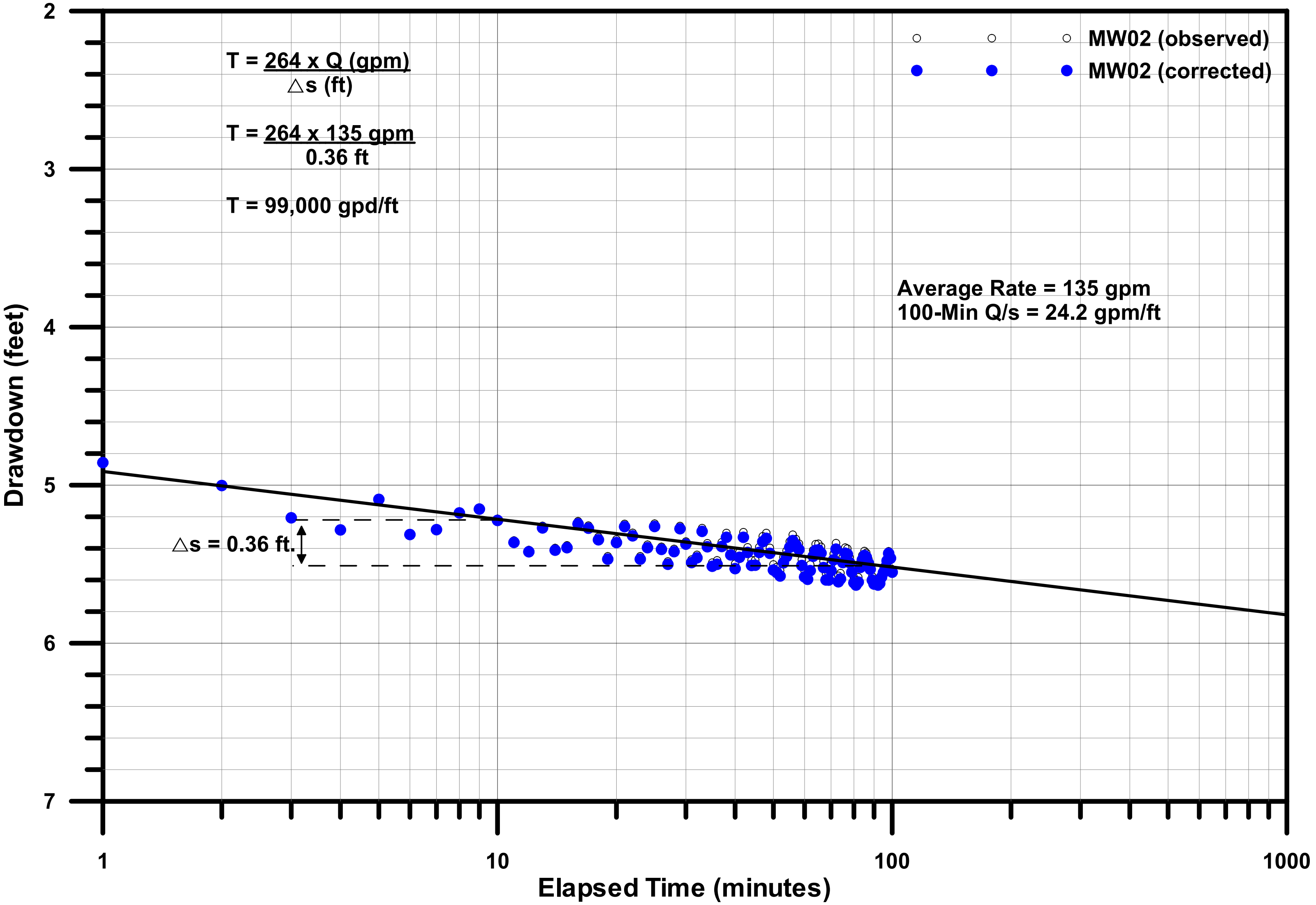


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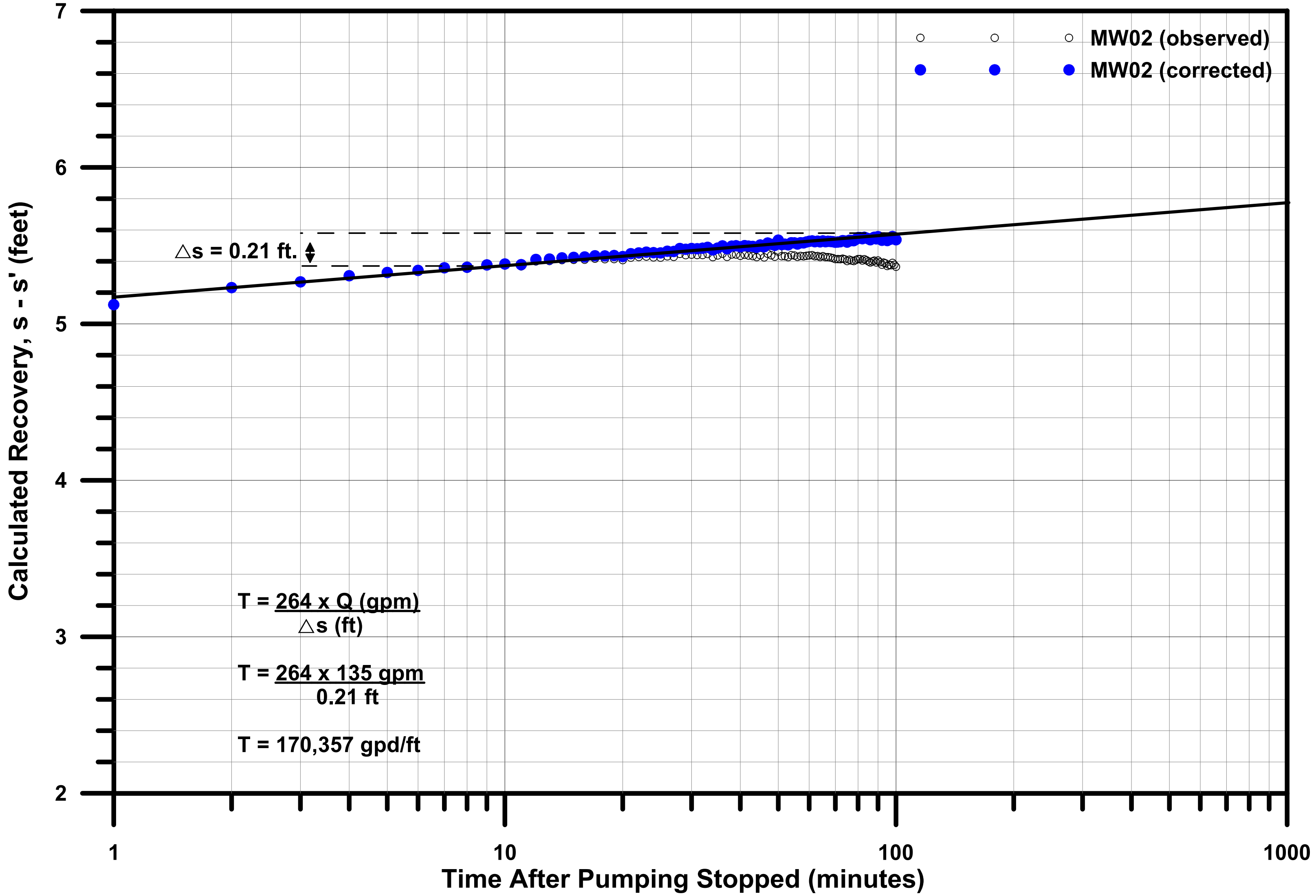
FIGURE B29. MCWP-MW02 POST-INJECTION PUMPING TEST - MW02 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{264 \times Q\ (gpm)}{\triangle s\ (ft)}$$

$$T = \frac{264 \times 135\ gpm}{0.21\ ft}$$

T = 170,357 gpd/ft

FIGURE B30. MCWP-MW02 POST-INJECTION PUMPING TEST - MW02 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

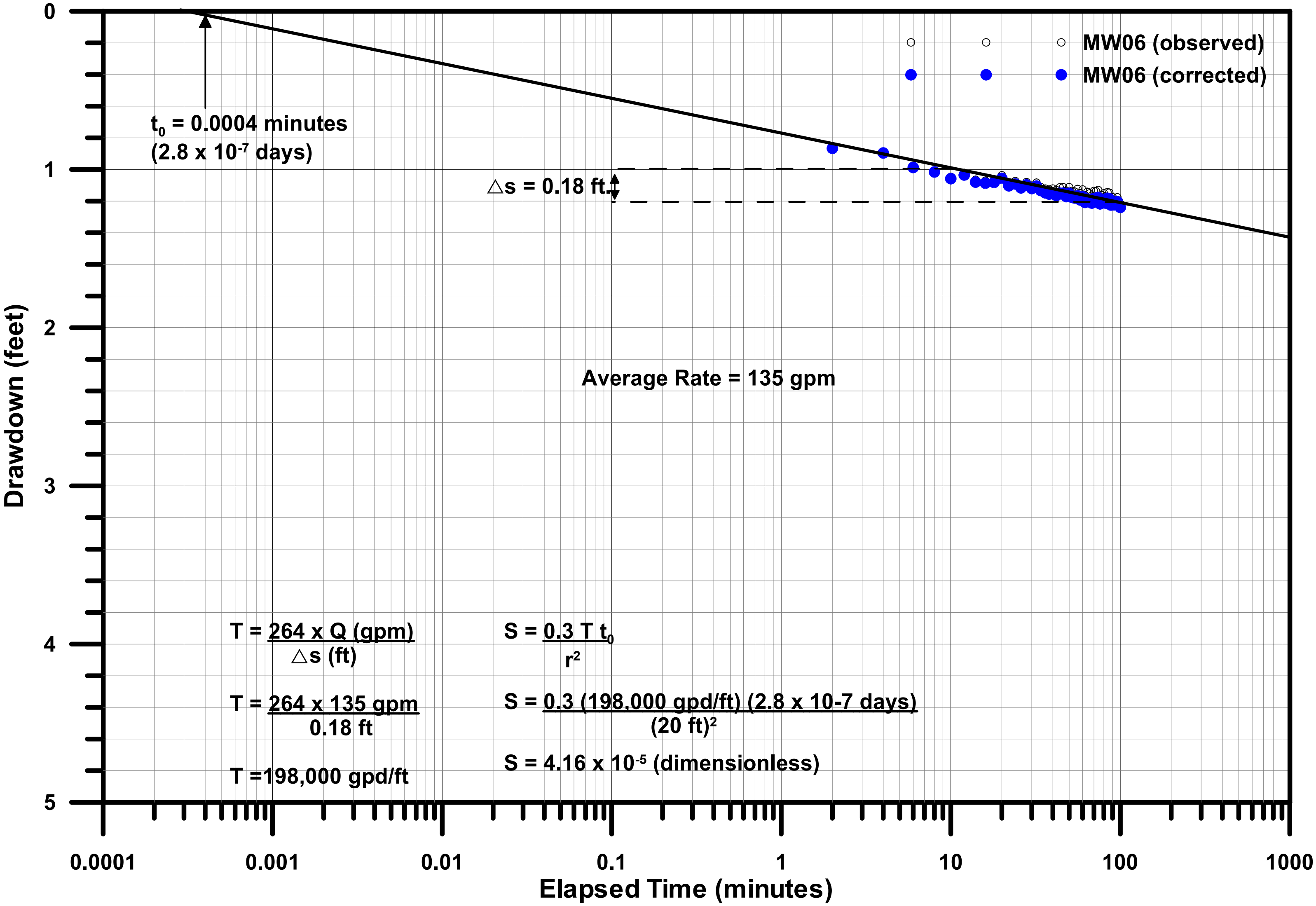
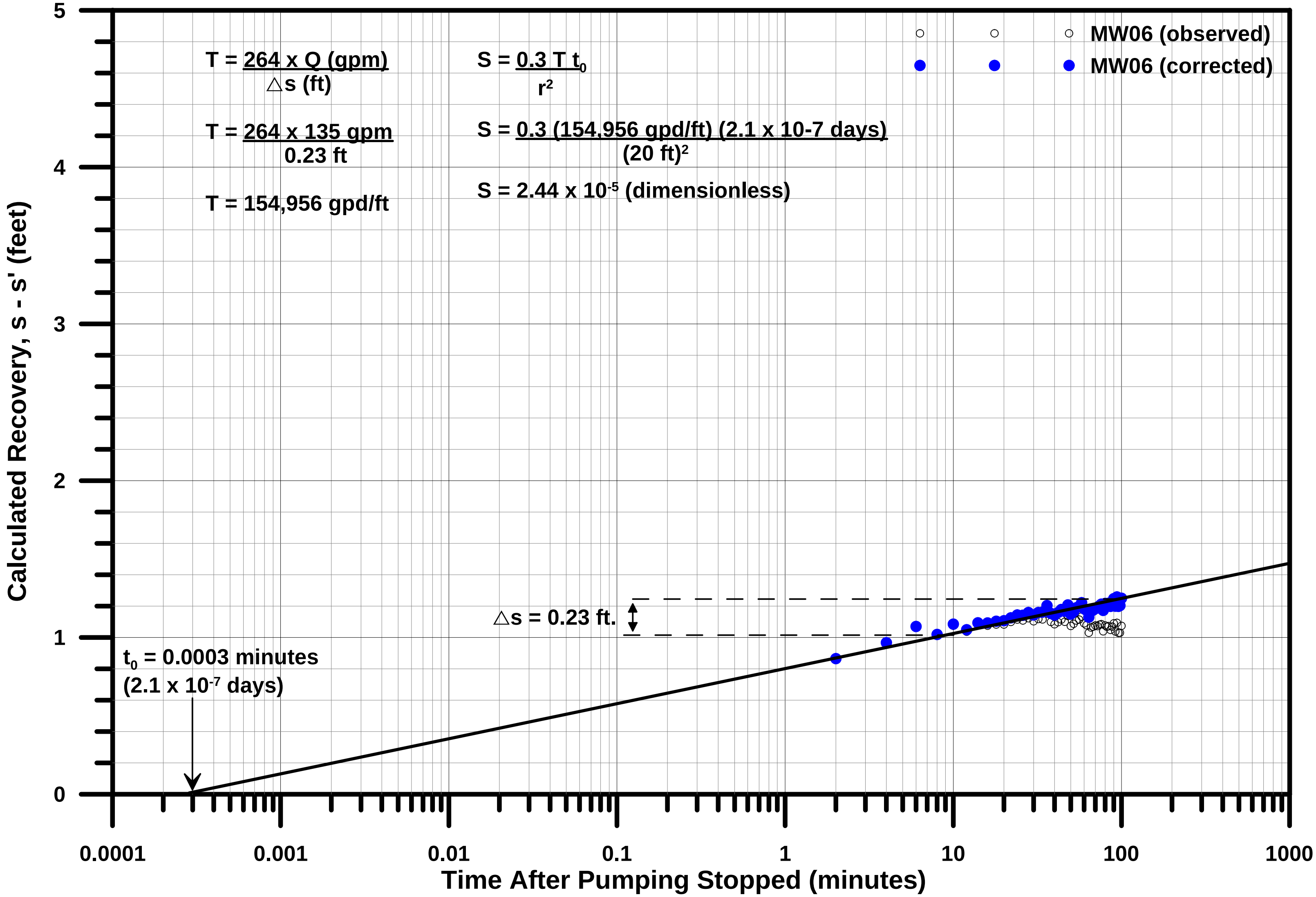
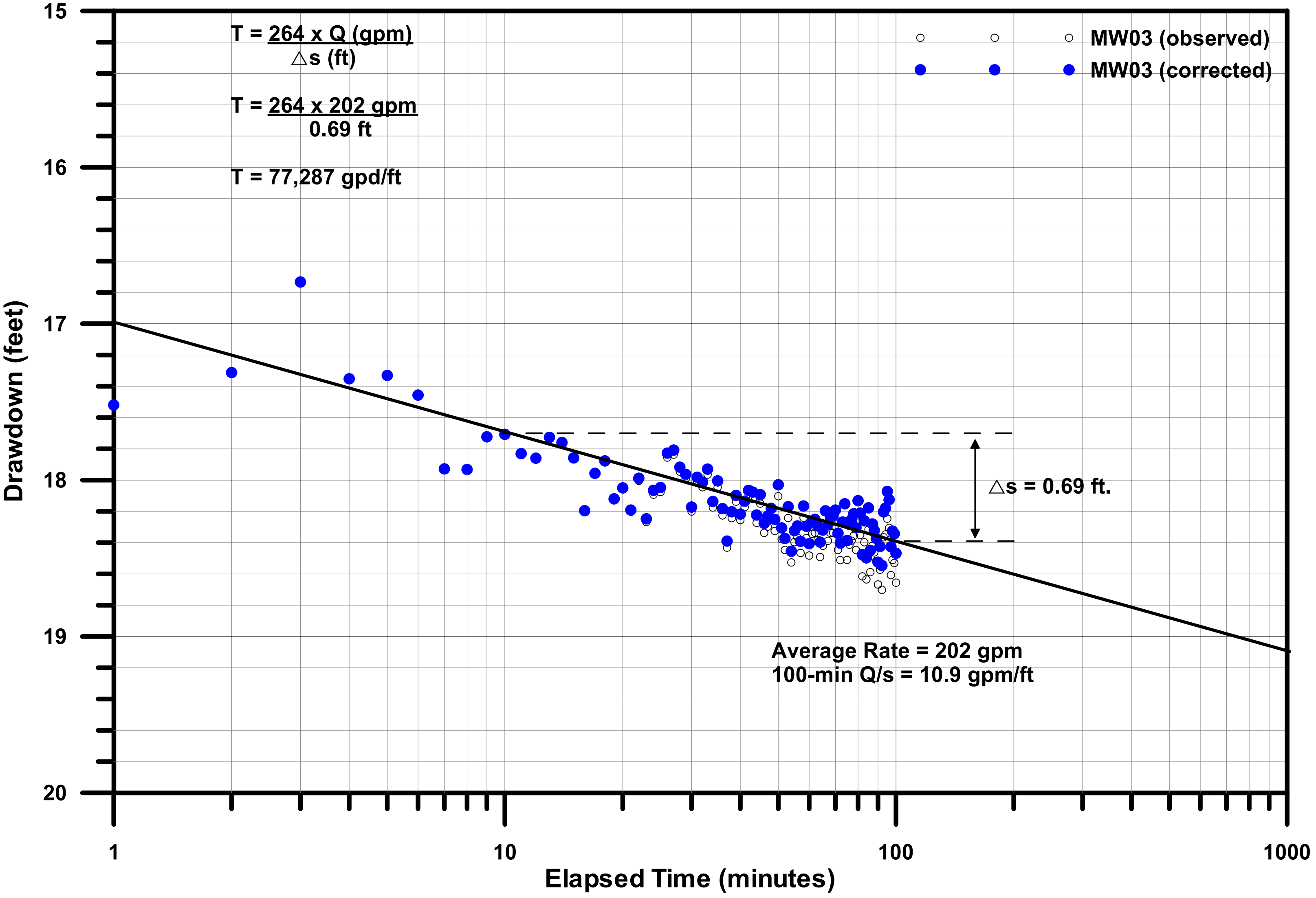


FIGURE B31. MCWP-MW02 POST-INJECTION PUMPING TEST - MW06 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO
water resources

FIGURE B32. MCWP-MW02 POST-INJECTION PUMPING TEST - MW06 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B33. MCWP-MW03 PRE-INJECTION PUMPING TEST - MW03 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

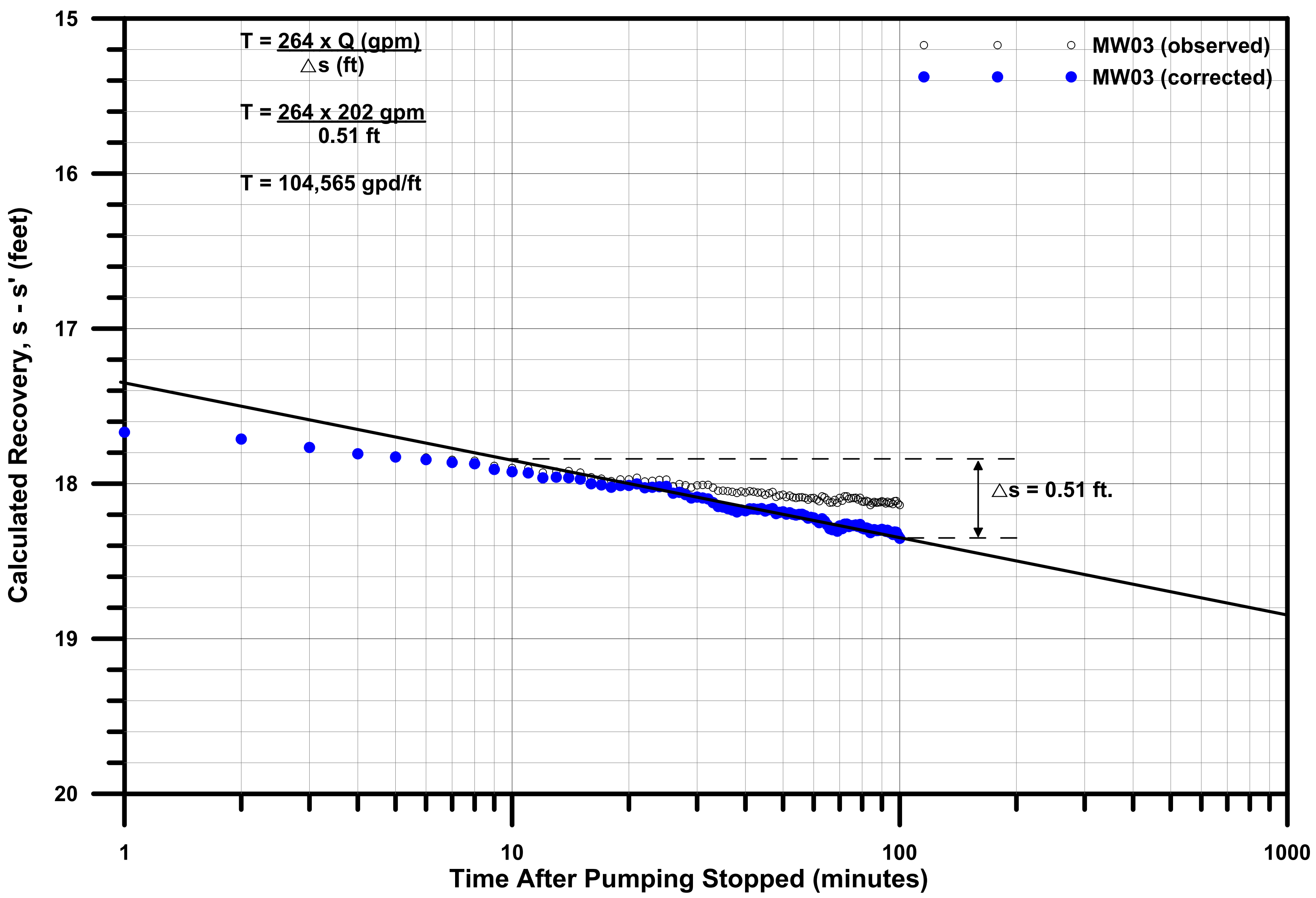
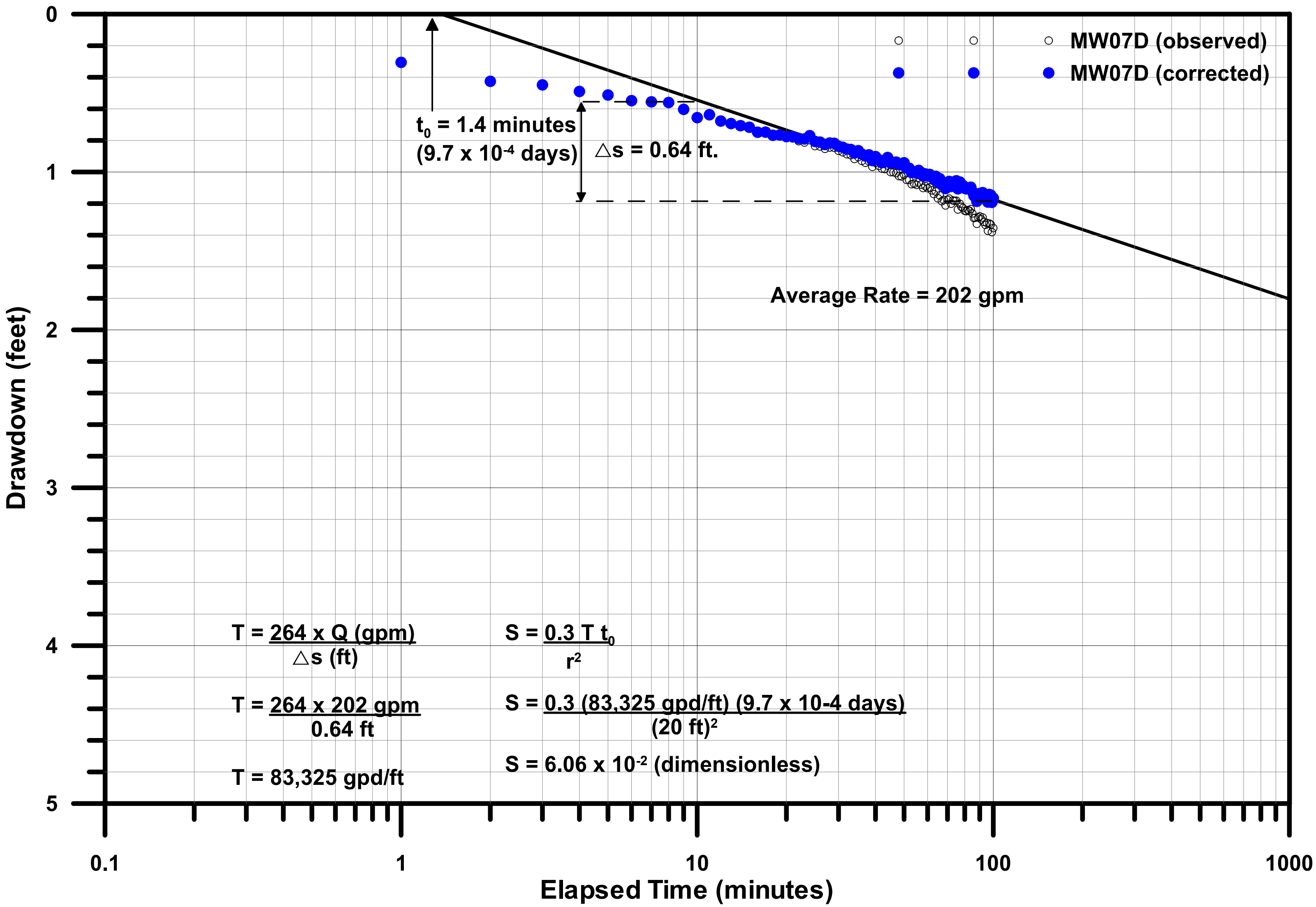
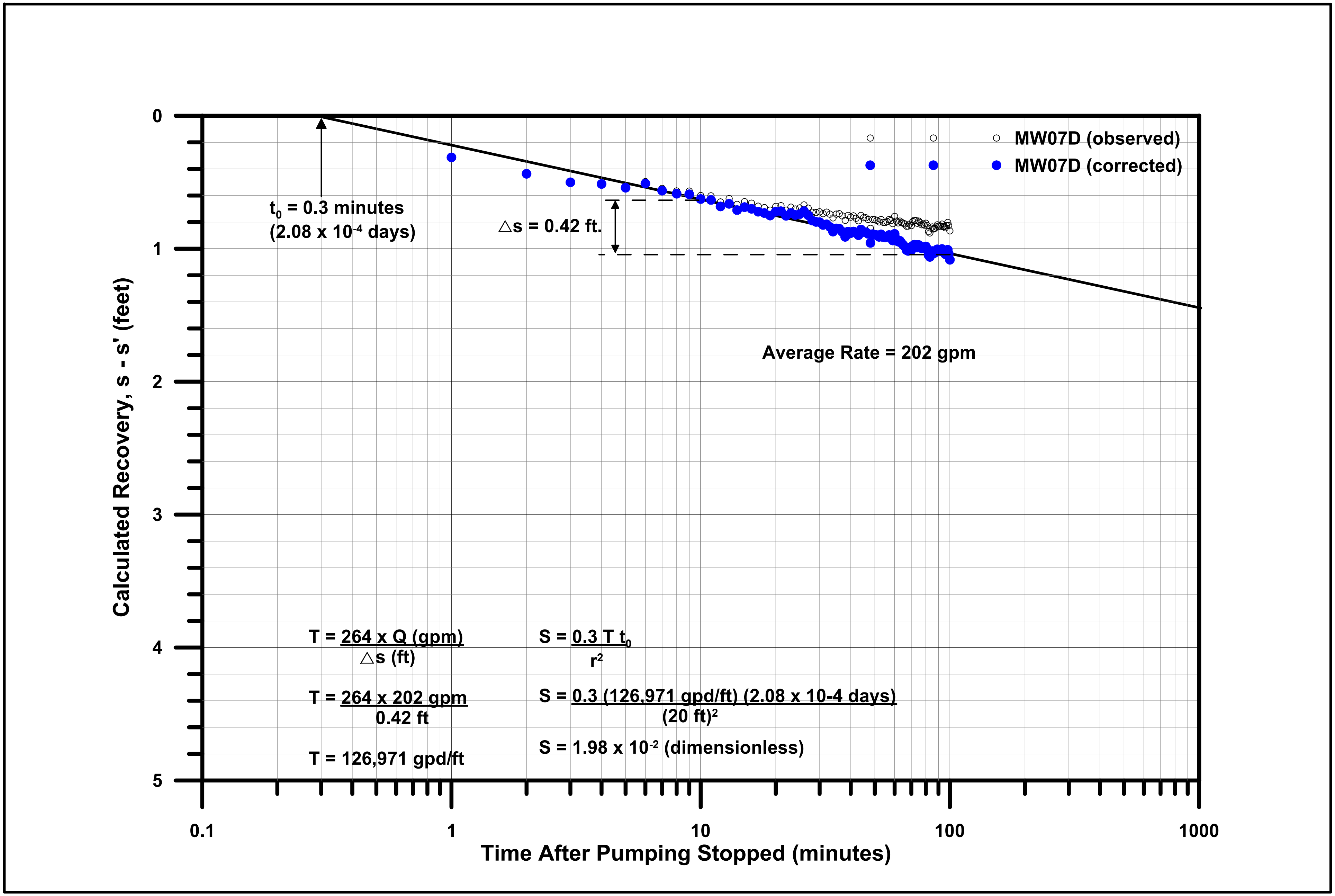


FIGURE B34. MCWP-MW03 PRE-INJECTION PUMPING TEST - MW03 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



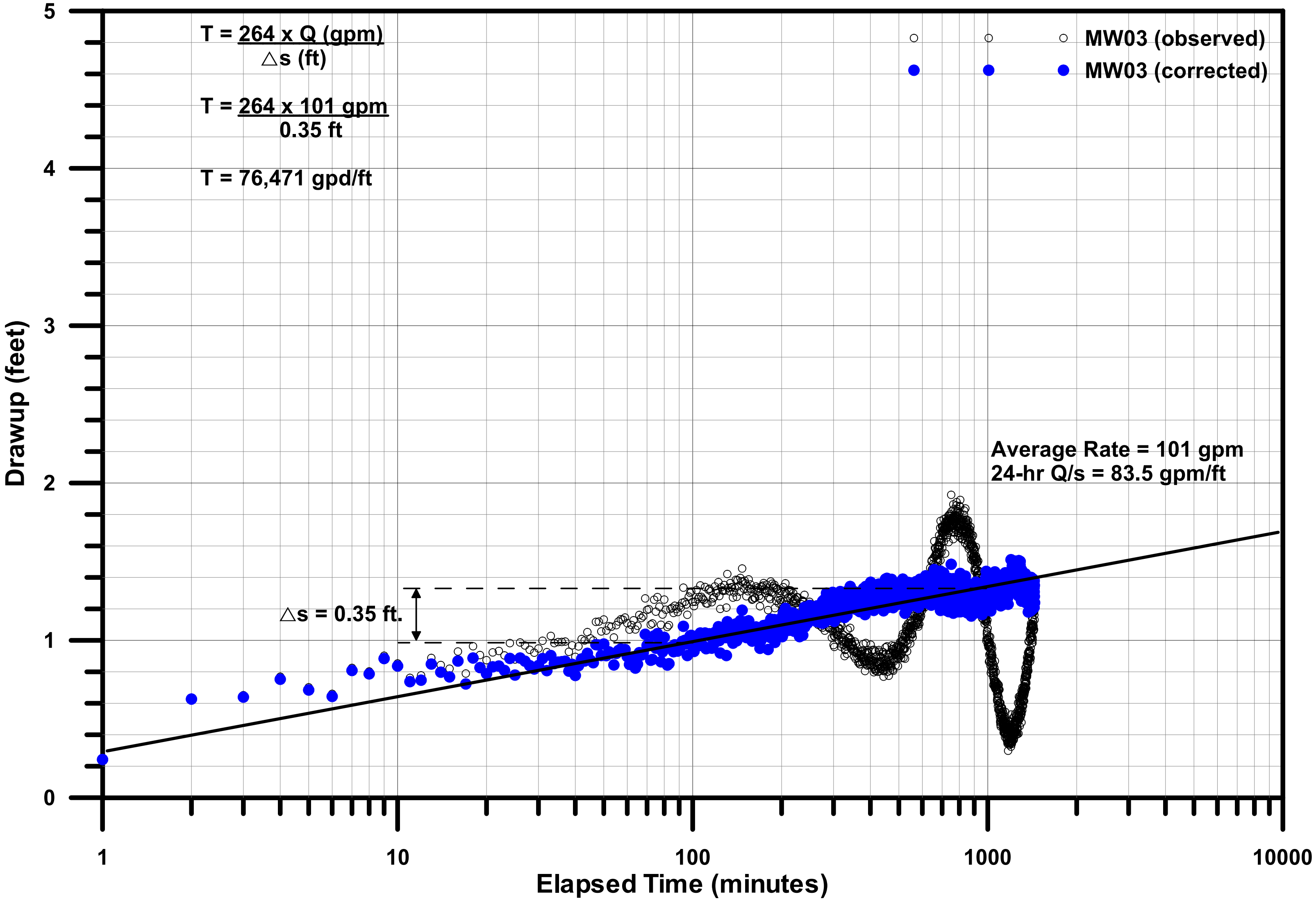
PUEBLO
water resources

FIGURE B35. MCWP-MW03 PRE-INJECTION PUMPING TEST - MW07D DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



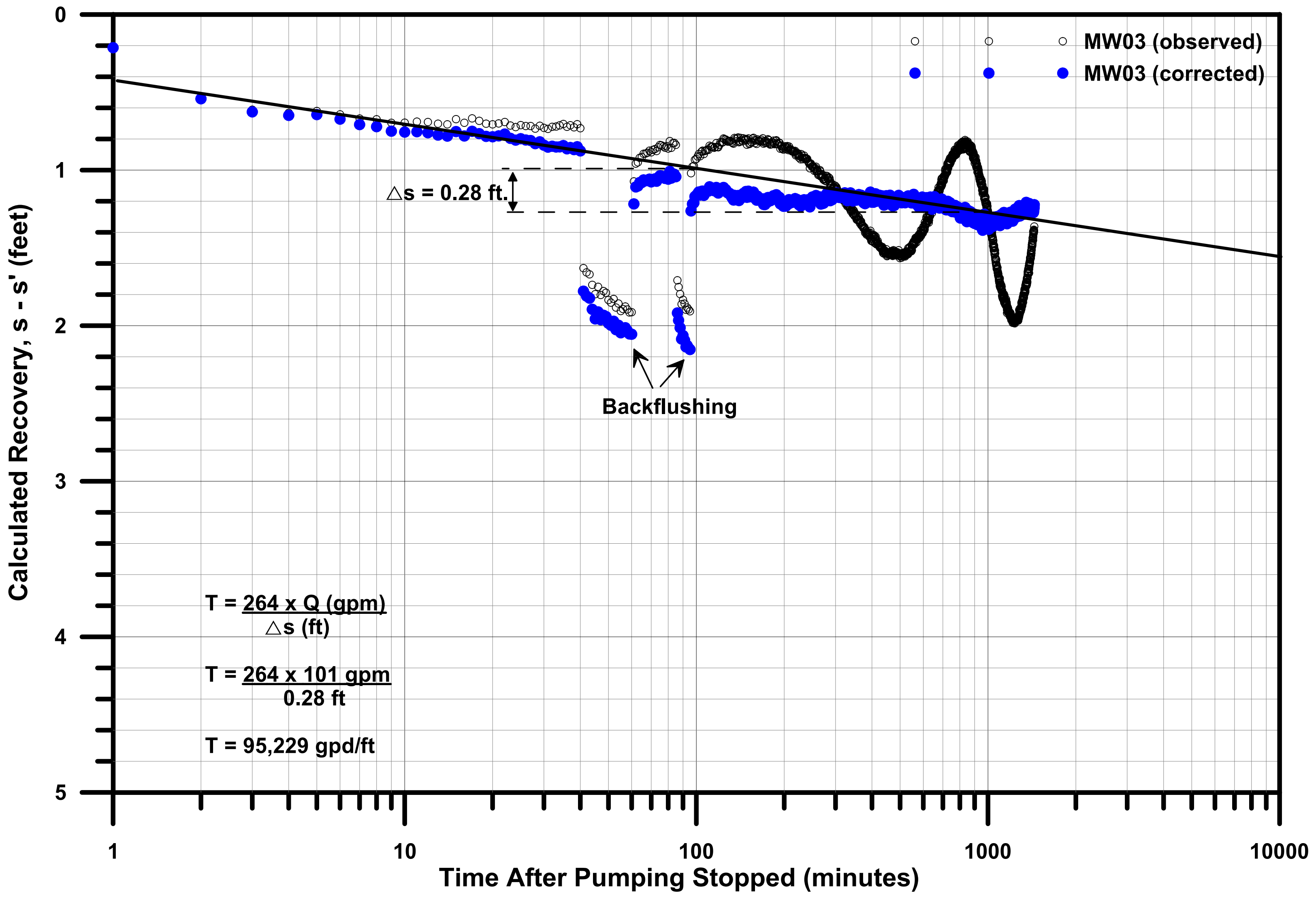
PUEBLO
water resources

FIGURE B36. MCWP-MW03 PRE-INJECTION PUMPING TEST - MW07D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B37. MCWP-MW03 24-HR INJECTION TEST - MW03 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



T = 264 x Q (gpm) / △s (ft)

T = 264 x 101 gpm / 0.28 ft

T = 95,229 gpd/ft

FIGURE B38. MCWP-MW03 24-HR INJECTION TEST - MW03 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

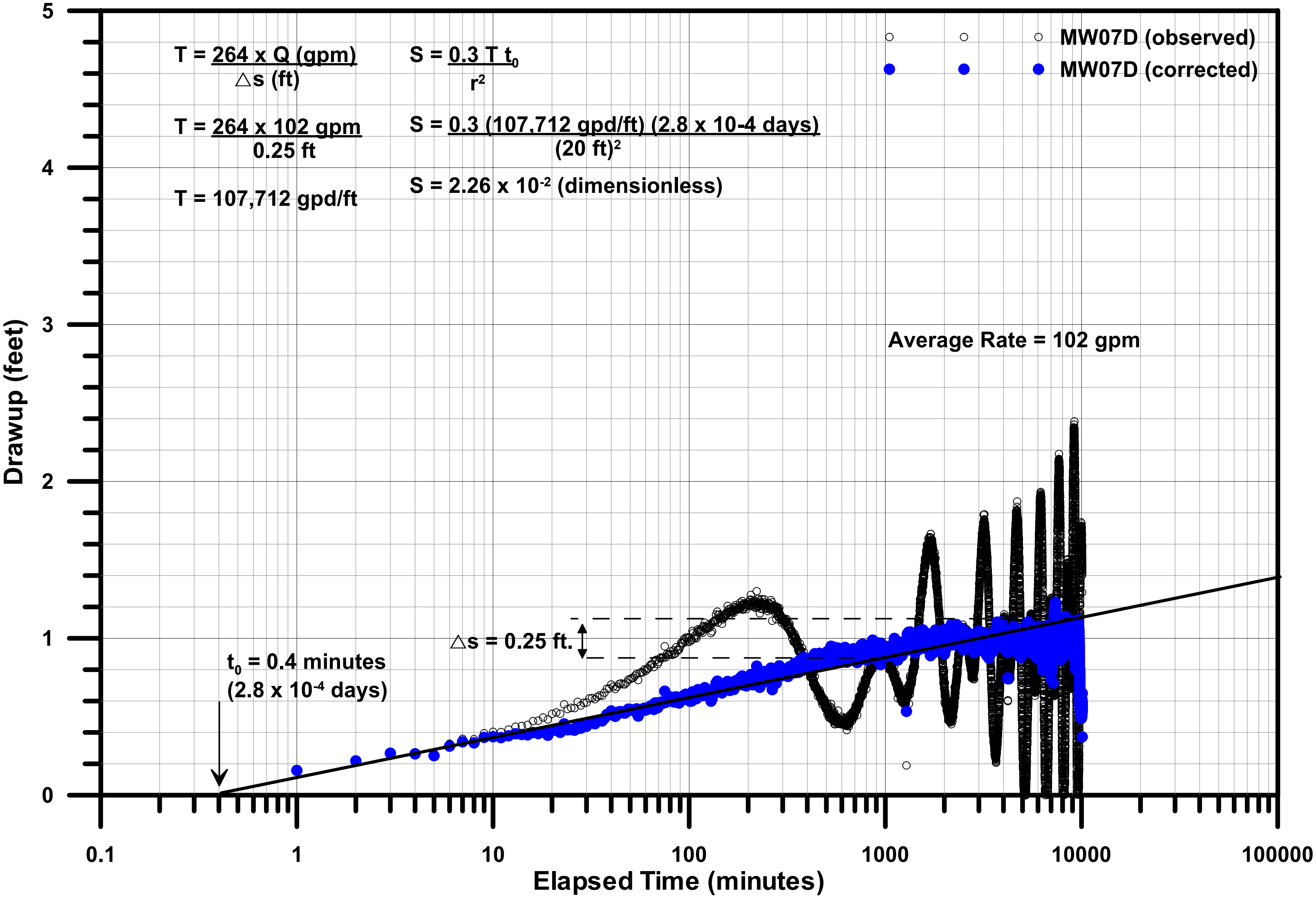


FIGURE B39. MCWP-MW03 24-HR INJECTION TEST - MW07D DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

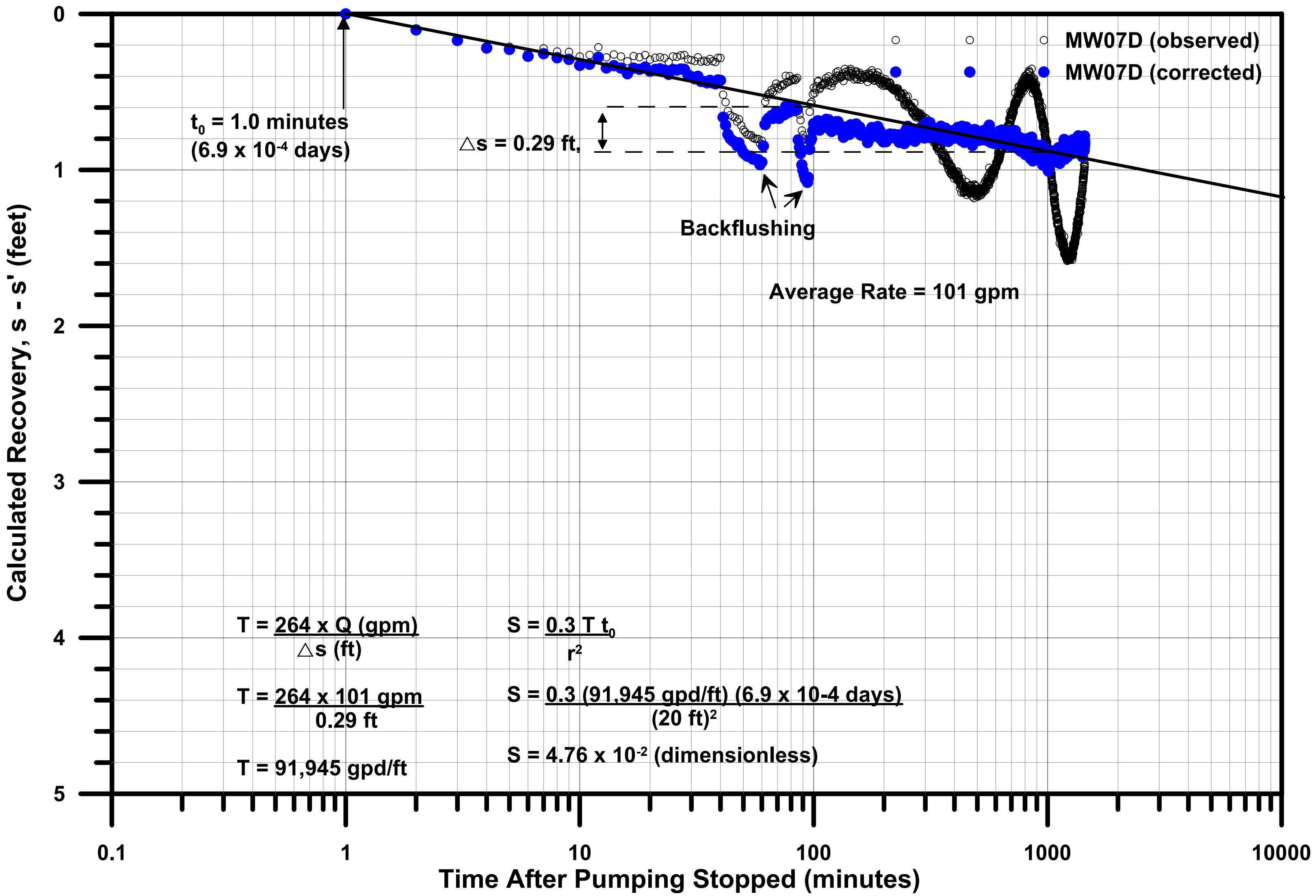
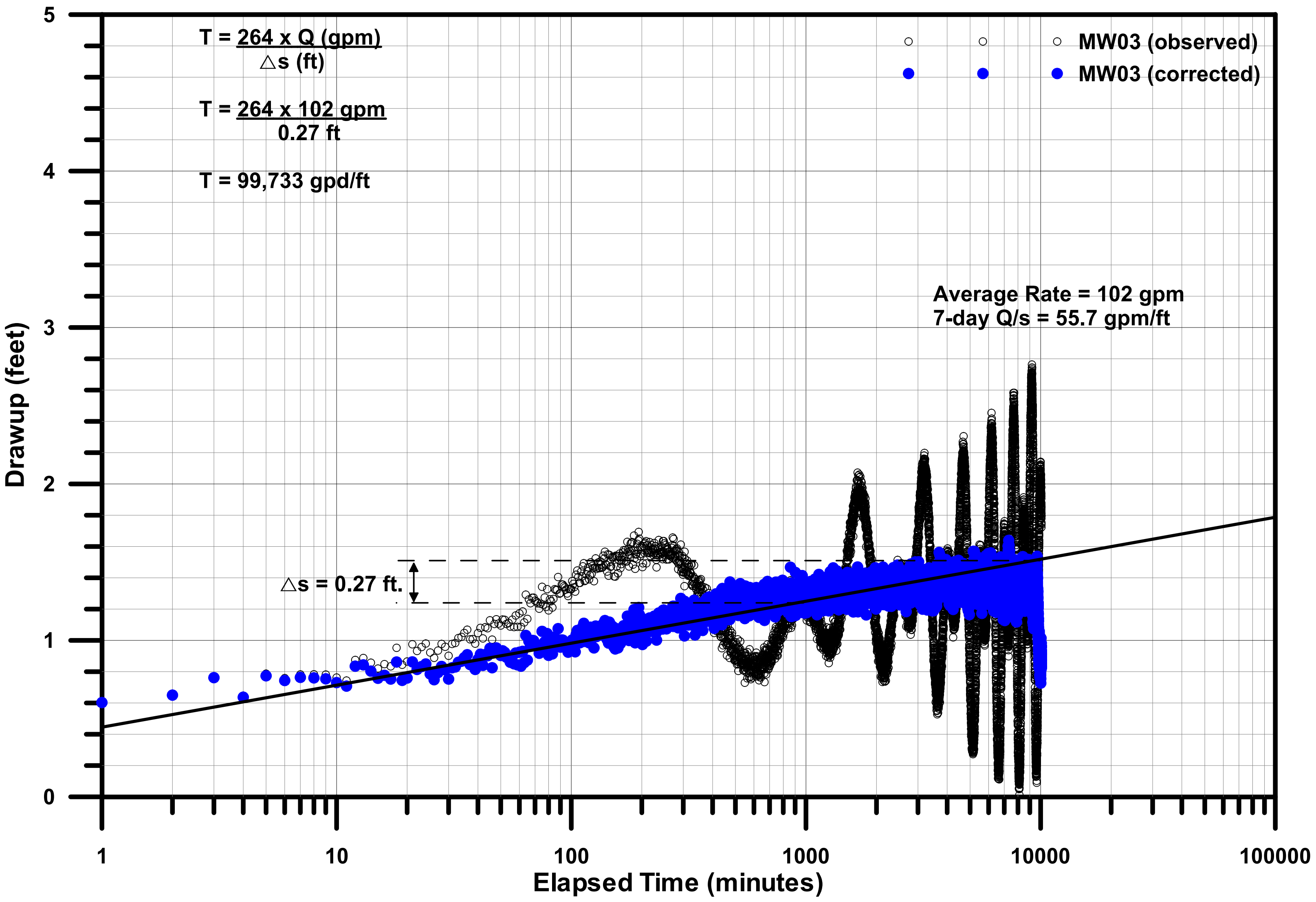
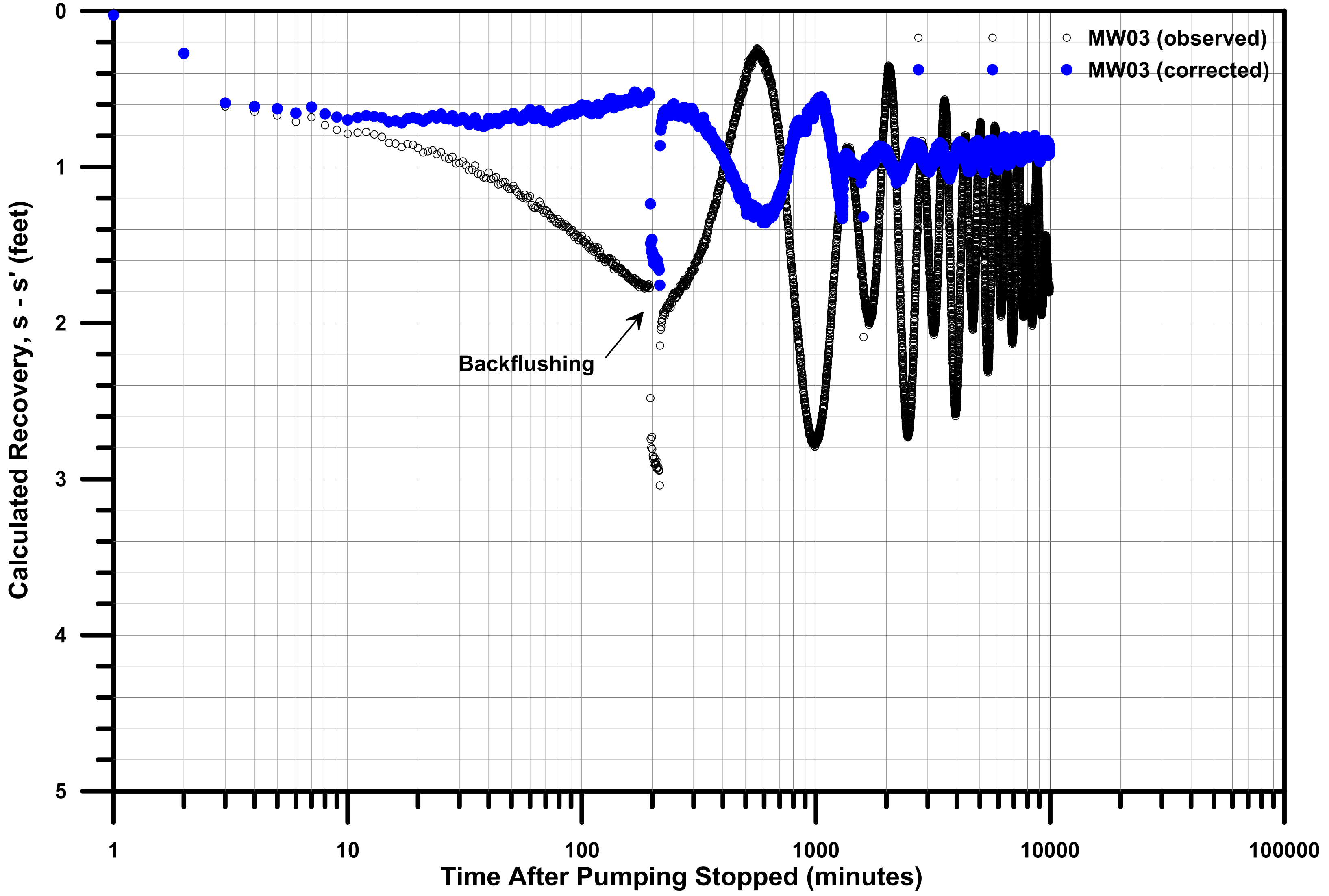


FIGURE B40. MCWP-MW03 24-HR INJECTION TEST - MW07D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B41. MCWP-MW03 7-DAY INJECTION TEST - MW03 DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B42. MCWP-MW03 7-DAY INJECTION TEST - MW03 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

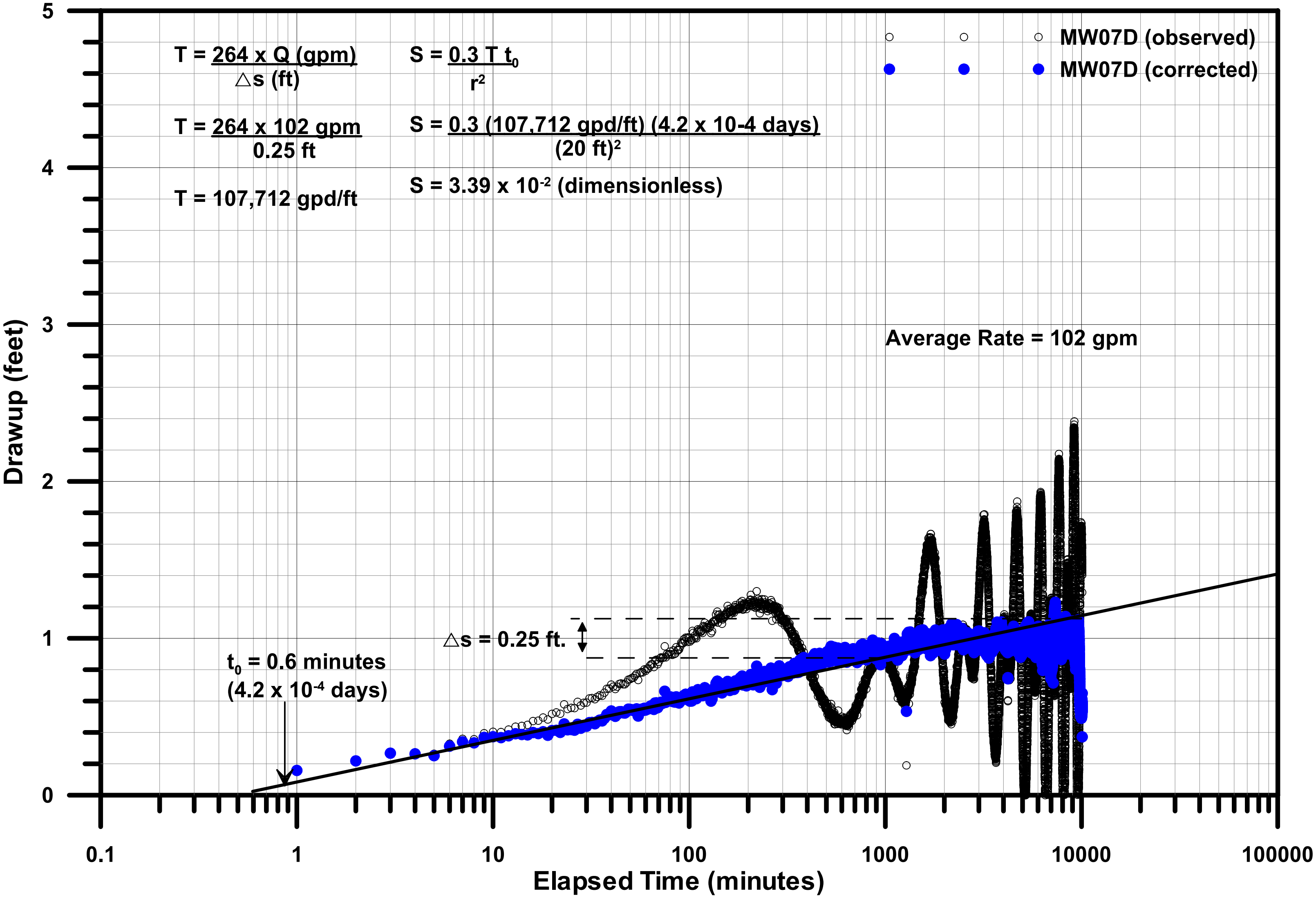
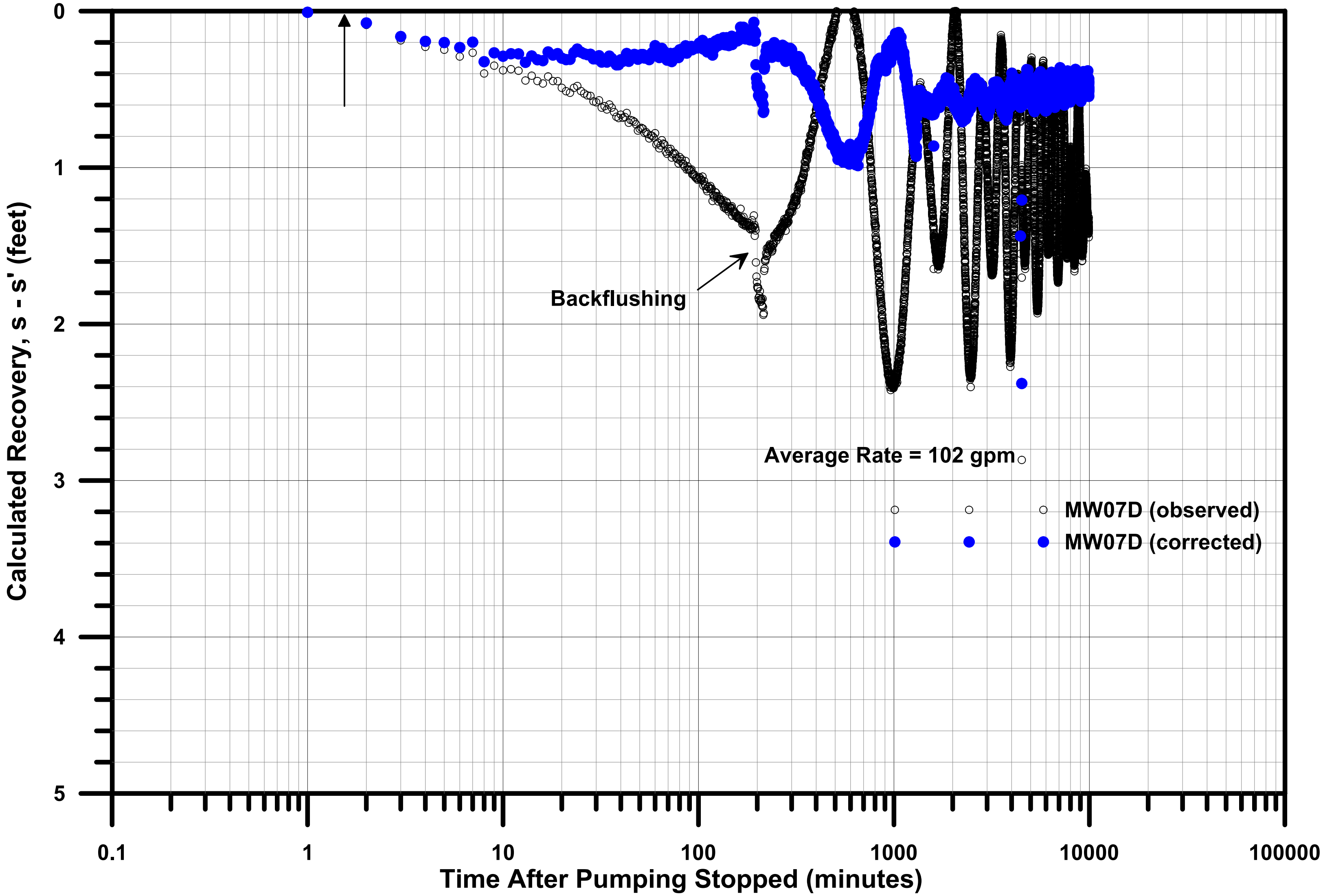


FIGURE B43. MCWP-MW03 7-DAY INJECTION TEST - MW07D DRAWUP DATA

Malibu Groundwater Injection Feasibility Project - Phase 3

RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B44. MCWP-MW03 7-DAY INJECTION TEST - MW07D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

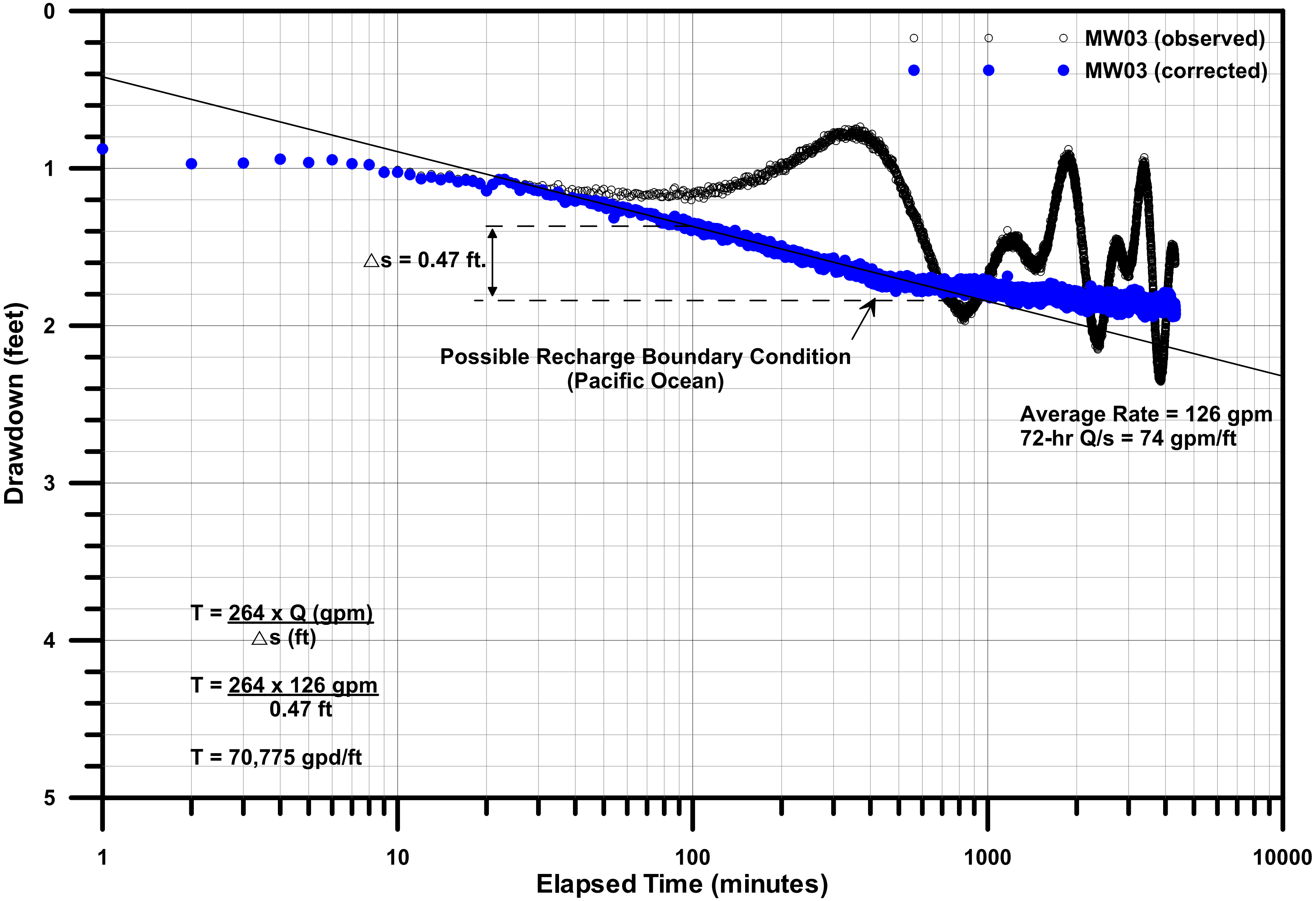
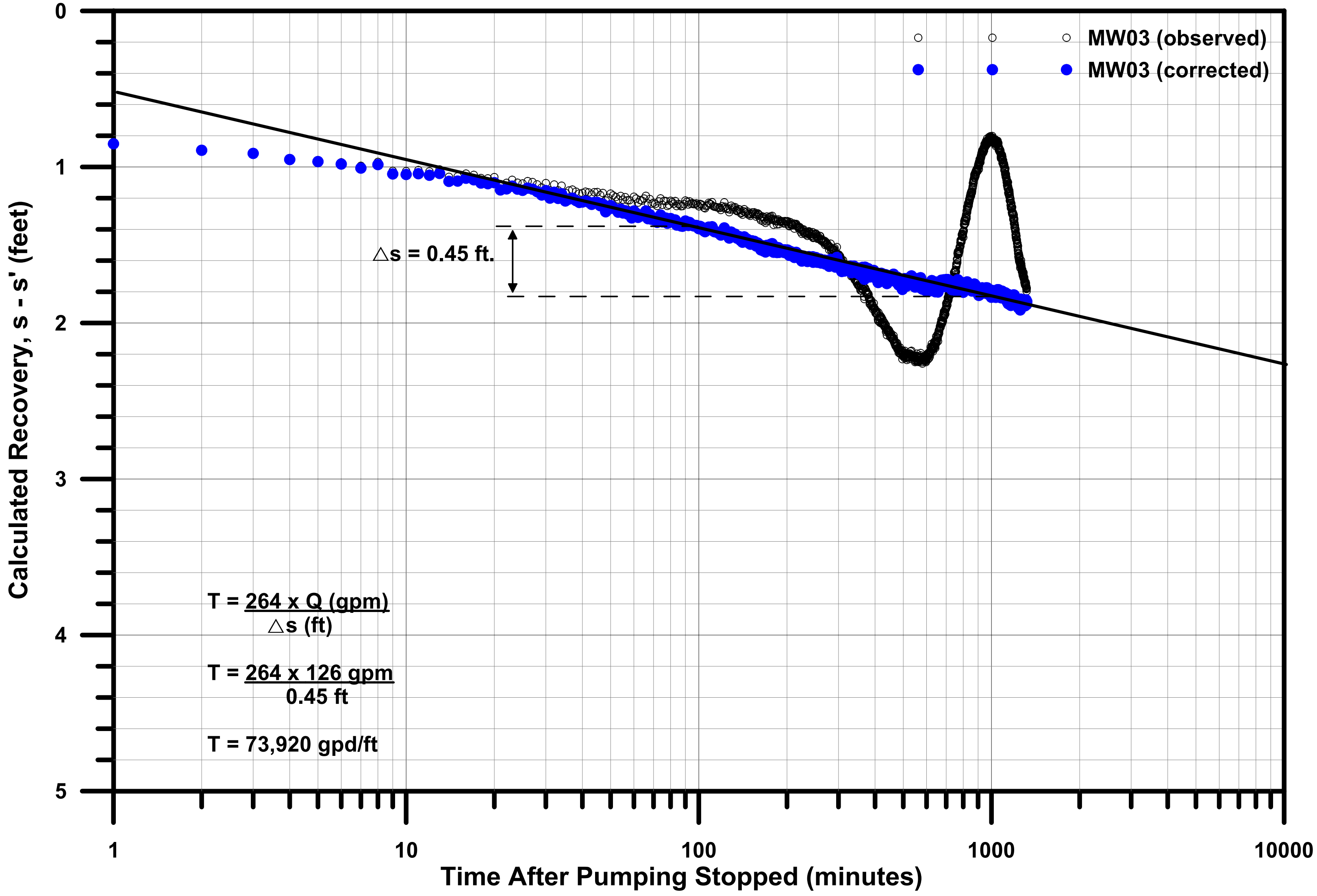


FIGURE B45. MCWP-MW03 72-HR PUMPING TEST - MW03 DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



T = $\frac{264 \times Q \text{ (gpm)}}{\triangle s \text{ (ft)}}$

T = $\frac{264 \times 126 \text{ gpm}}{0.45 \text{ ft}}$

T = 73,920 gpd/ft

FIGURE B46. MCWP-MW03 72-HR PUMPING TEST - MW03 RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

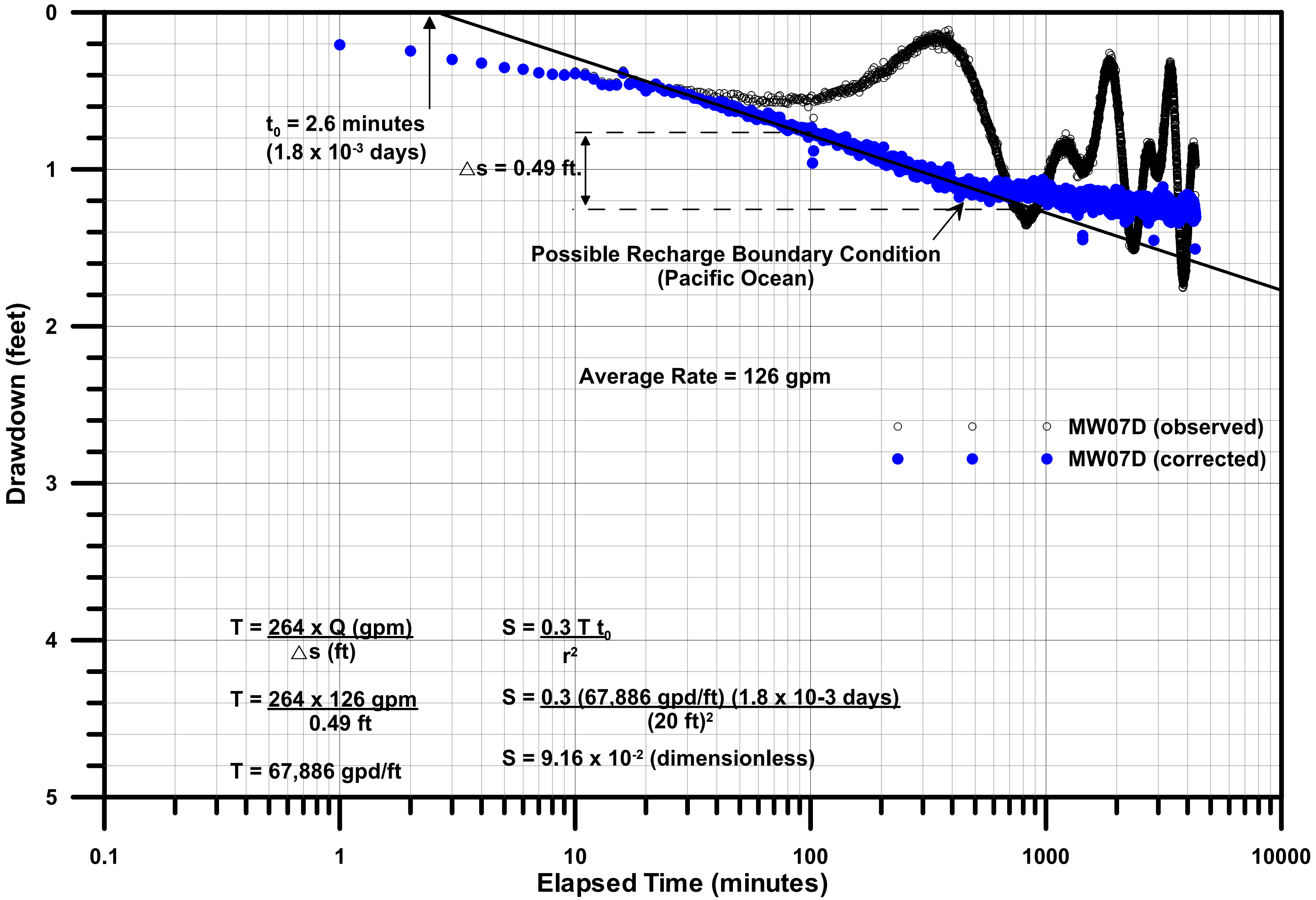
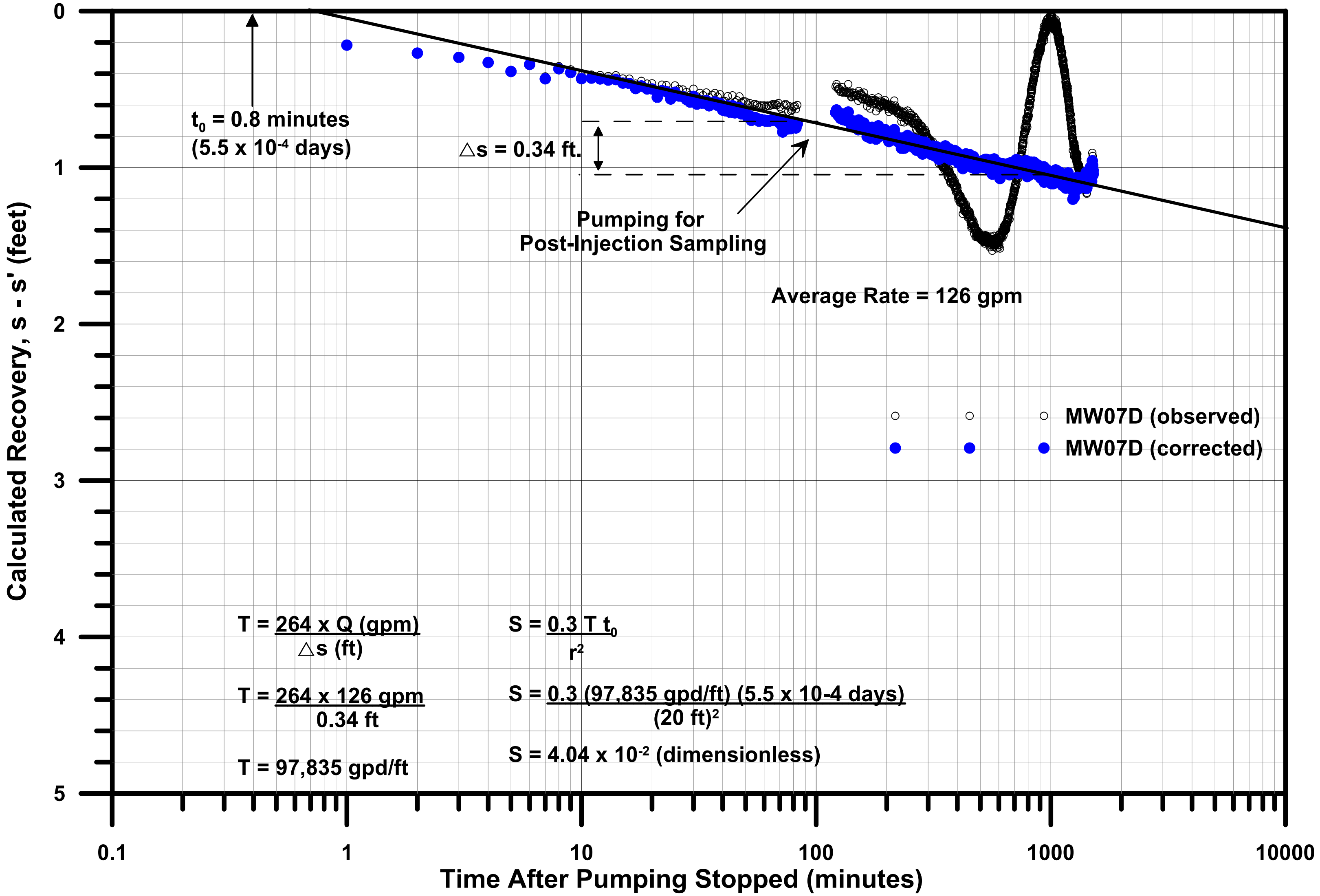


FIGURE B47. MCWP-MW03 72-HR PUMPING TEST - MW07D DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{264 \times Q\ (\text{gpm})}{\triangle s\ (\text{ft})}$$

$$T = \frac{264 \times 126\ \text{gpm}}{0.34\ \text{ft}}$$

T = 97,835 gpd/ft

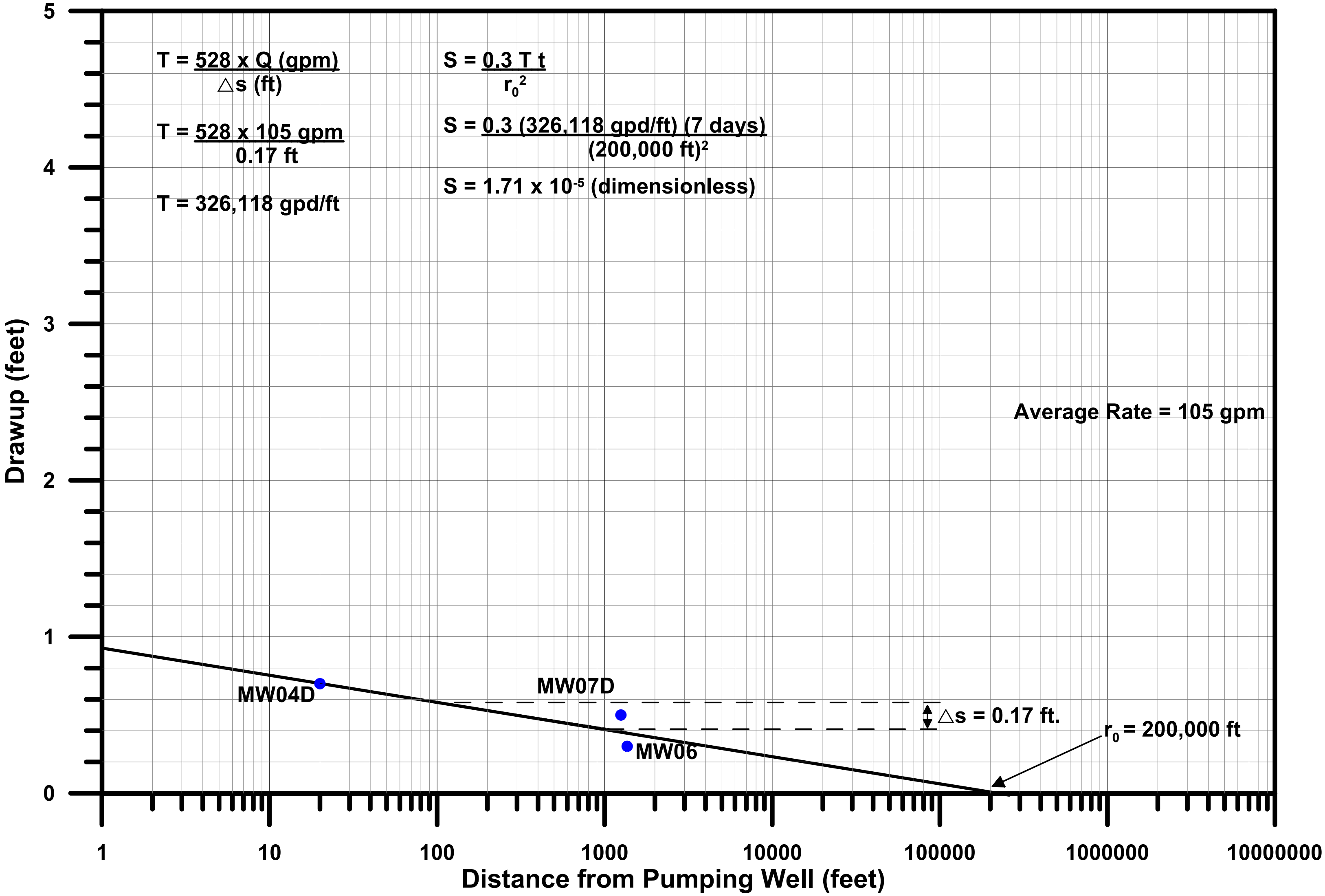
$$S = \frac{0.3\ T\ t_0}{r^2}$$

$$S = \frac{0.3\ (97{,}835\ \text{gpd/ft})\ (5.5 \times 10\text{-}4\ \text{days})}{(20\ \text{ft})^2}$$

S = 4.04×10^{-2} (dimensionless)

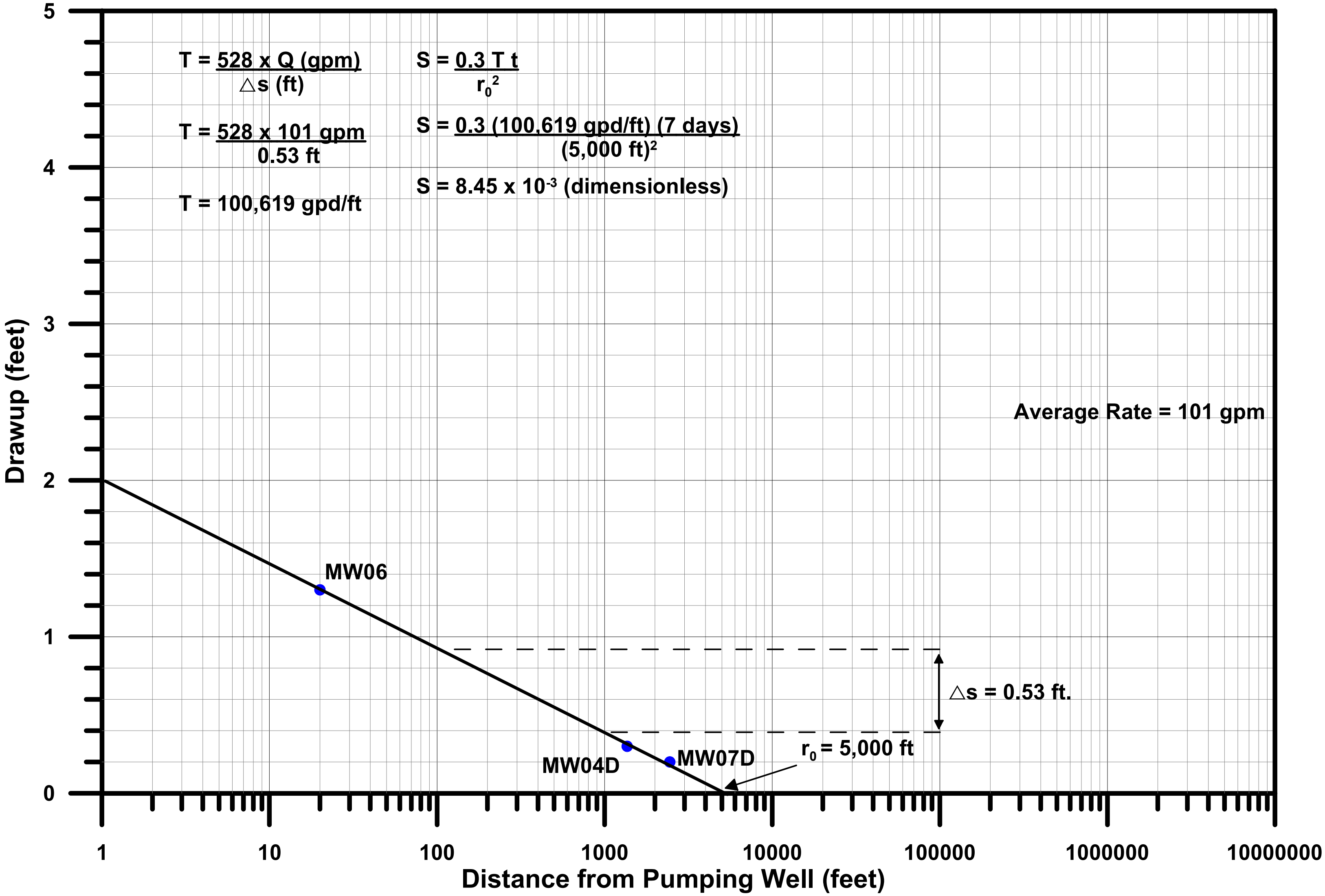
PUEBLO
water resources

FIGURE B48. MCWP-MW03 72-HR PUMPING TEST - MW07D RECOVERY DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



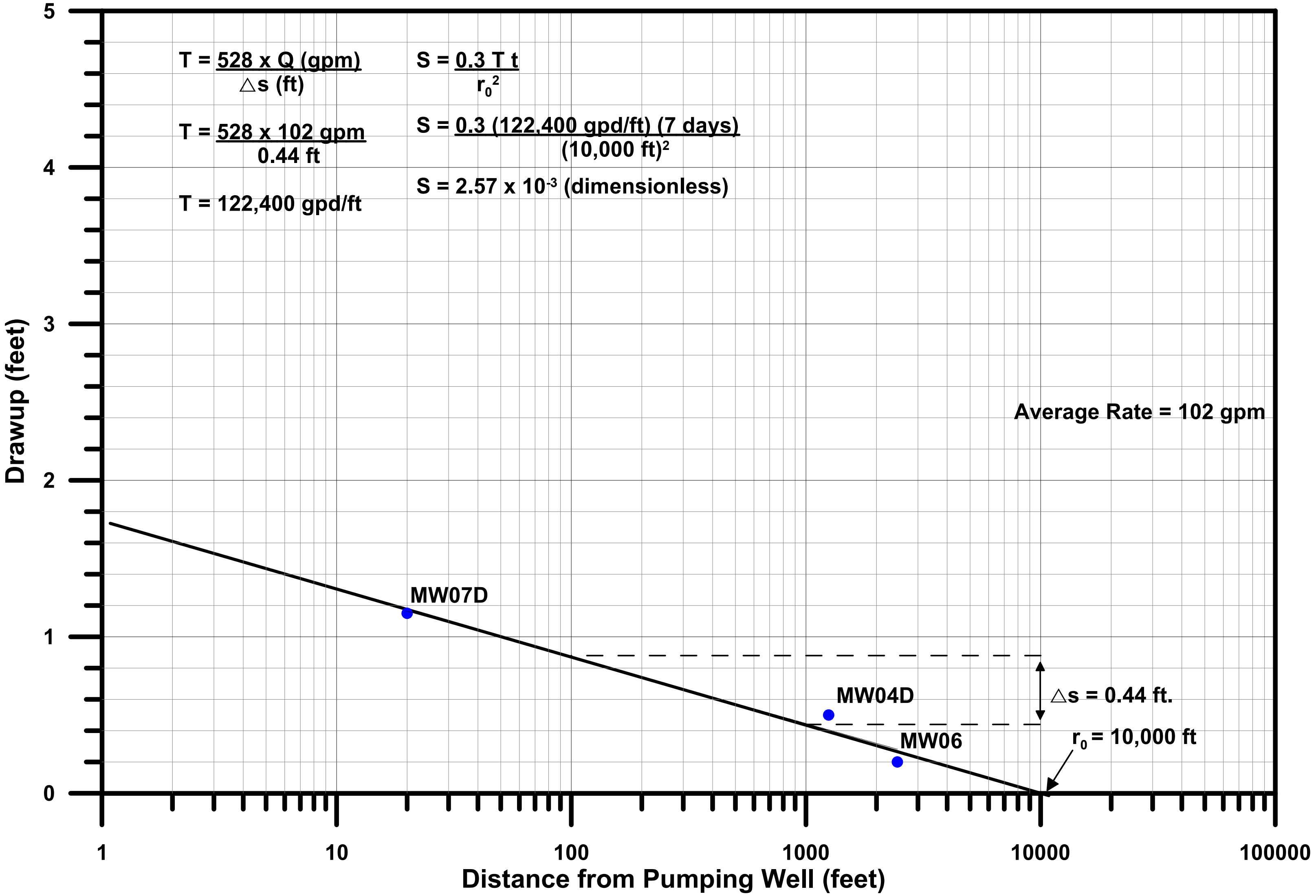
PUEBLO
water resources

FIGURE B49. MCWP-MW01 7-DAY INJECTION TEST - DISTANCE VS. DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



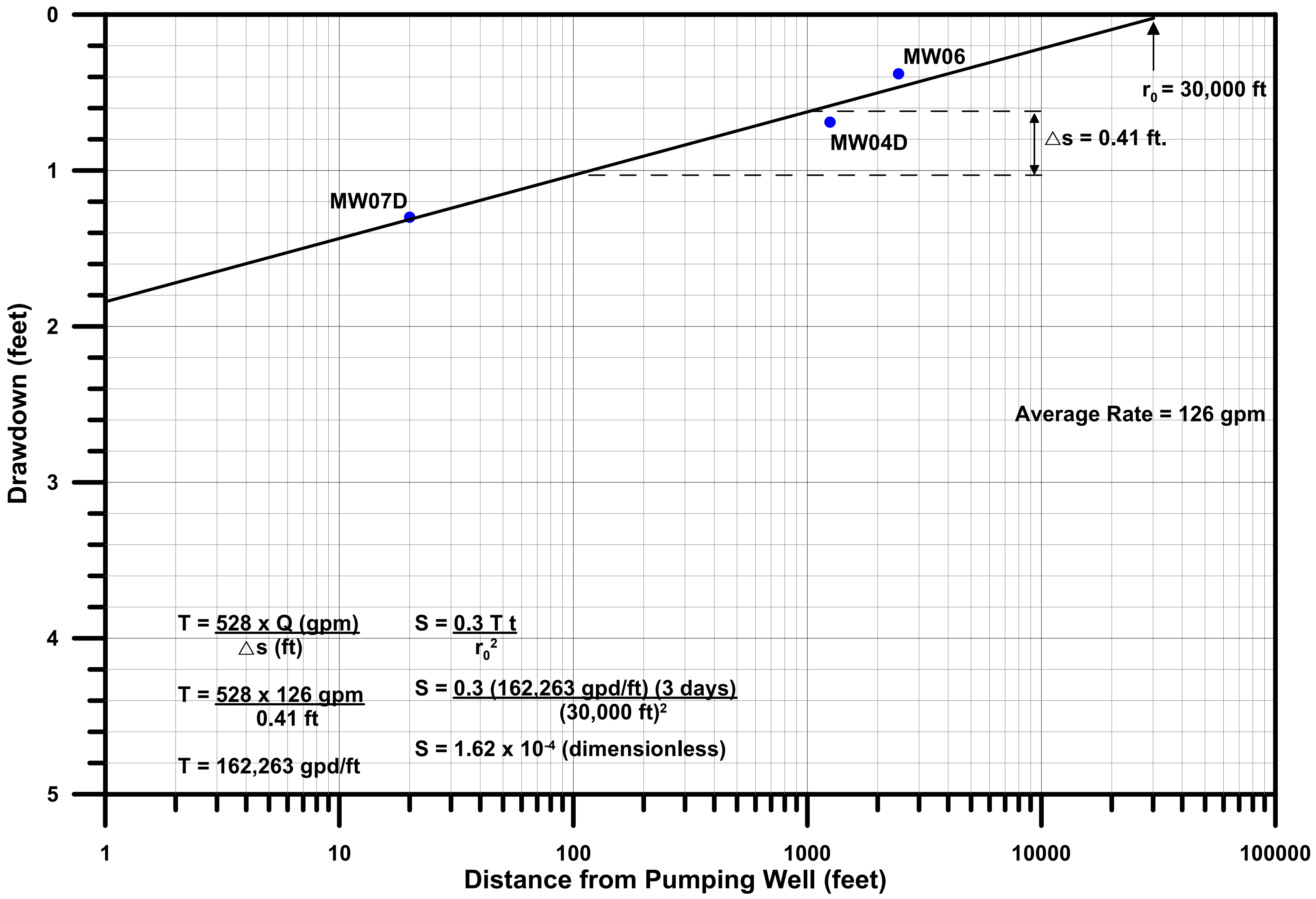
PUEBLO
water resources

FIGURE B50. MCWP-MW02 7-DAY INJECTION TEST - DISTANCE VS. DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



PUEBLO water resources

FIGURE B51. MCWP-MW03 7-DAY INJECTION TEST - DISTANCE VS. DRAWUP DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu



$$T = \frac{528 \times Q\ (\text{gpm})}{\triangle s\ (\text{ft})}$$

$$T = \frac{528 \times 126\ \text{gpm}}{0.41\ \text{ft}}$$

T = 162,263 gpd/ft

$$S = \frac{0.3\ T\ t}{r_0^2}$$

$$S = \frac{0.3\ (162{,}263\ \text{gpd/ft})\ (3\ \text{days})}{(30{,}000\ \text{ft})^2}$$

$S = 1.62 \times 10^{-4}$ (dimensionless)

PUEBLO
water resources

FIGURE B52. MCWP-MW03 72-HR PUMPING TEST - DISTANCE VS. DRAWDOWN DATA
Malibu Groundwater Injection Feasibility Project - Phase 3
RMC Water and Environment / City of Malibu

TECHNICAL MEMORANDUM

Pueblo Water Resources, Inc.
4478 Market St., Suite 705 Tel: 805.644.0470
Ventura, CA 93003 Fax: 805.644.0480

To:	RMC Water and Environment	Date:	March 24, 2014
Attention:	Leslie Dumas, P.E. Senior Water Resources Engineer	Project No:	12-0051
Copy to:			
From:	Stephen Tanner, P.E. Principal Engineer		
Subject:	Malibu Groundwater Injection Feasibility Project – Phase 3; Geochemical Modeling Assessment		

INTRODUCTION

Attached please find our geochemical modeling assessment report for the proposed recycled water injection component of the City of Malibu's (City's) Civic Center Wastewater Treatment Facility (CCWTF) project. The purpose of this Technical Memorandum (TM) is to provide an overview of the data and methods used in our geochemical analysis, and to explain the significance of major findings of the evaluation program.

The proposed project would involve the use of specially designed injection wells as a means to dispose of disinfected tertiary-treated wastewater produced at the City's proposed Civic Center Wastewater Treatment Facility (CCWTF) into the underlying Malibu Valley Groundwater Basin. The goal of the project is to mitigate undesirable consequences of historical direct disposal (i.e., via septic systems) of commercial and domestic septic sewage on the local environment.

The feasibility of disposing of large quantities of recycled water via injection wells is critically dependent upon the process of mixing and displacement of the native ground water (NGW) by the injection source water (i.e., the CCWTF treated effluent). Under certain circumstances, adverse physical and geochemical reactions can occur which would reduce or inhibit injection operations, reduce the life of the wells, or leach undesirable compounds from the geologic matrix of the aquifer minerals.

In an effort to understand and quantify the extent and potential for such reactions to occur (or not), we performed a series of geochemical modeling assessments of the individual waters and their mixing within a simulated subsurface environment representing the local Civic Center Gravels (CCG) aquifer. Data collected and utilized for the modeling analyses included the following:

- Lithologic and mineralogical data from samples of the geologic matrix of project test well borings in the target aquifer (to represent the aquifer matrix composition);

- Water-quality samples collected from the project test wells MCWP-MW01, -MW02, and –MW03 prior to injection testing (to represent the NGW composition);
- Water-quality samples of MBR-treated effluent from a local wastewater treatment plant (known as the Lumber Yard Wastewater Treatment Facility) to represent as a surrogate the future treated effluent from the CCWWFT.

FINDINGS

METHOD OF ANALYSIS

The water and soil analyses were input into USGS's well known and well-documented geochemical equilibrium modeling program PHREEQC (version 2.18) and the Lawrence Livermore National Laboratory equilibrium database (1-10-2010 version). The major steps in the evaluation of the process included the following:

1. Evaluation of the quality and soundness of the analytic data sets to validate the reasonableness and accuracy of the input data to the model.
2. Evaluation of the geochemical character and state of equilibrium of each of the component waters (NGW and surrogate injectate) to determine their natural condition before mixing.
3. Simulation of mixing and displacement of the injection waters upon introduction to the aquifer, and subsequent evaluation of the equilibrium state of the resulting mixes.

PROGRAM RESULTS

1 – Evaluation of Data

The analytic data sets were evaluated in order to validate the reasonableness and accuracy of the input data to the model; anion/cation balances, method detection limits, analysis protocol deviations, and general chemistry conformity were all verified before modeling. The results of our assessment of the data are summarized below:

- In general, the water quality data from the NGW samples were found to be acceptable for use in the modeling work. Minor discrepancies were noted in detection limits and reporting protocols; however, the data were usable without correction or modification.
- The water quality from the surrogate treated effluent sampling (the 'Lumber Yard' effluent) was found to be reasonable with the exception of the analyses for the aqueous nutrient species of nitrogen compounds (TKN, NH3, T-N, and NO3) and the phosphorous compounds (T-P and PO4). These data were not only at odds with typical municipal treated waste effluent results, they were in disagreement with recent plant data collected over a full year of plant operations. Because these laboratory reported data were significantly different than the full year of results from the plant in 2012, it was determined that the 2012 historical dataset would be more appropriate for the modeling work.

- Anion/Cation balances for all water quality samples were reasonable and provided generally acceptable data for model input. There was a very slight outage of balance on MW-03, which is possibly explained by the discussion of MW-03 results below in Step 2 of the evaluation.

- The mineralogical analyses performed on the test boring samples were found to be well documented and conformed well with both typical values and internal QA/QC processes. There were no questionable results in the work.

2 – Evaluation of the Geochemical Character of Individual Components

Evaluation of the NGWs from the three test wells did not show any particularly problematic conditions. Specific highlights of the analyses and evaluation included the following:

- All three wells had redox values indicative of Fe(2+)/Fe(3+) coupled equilibrium, indicating that the ferrous/ferric transitional state was naturally present in the aquifer. This would be a likely result of the presence in excess iron in the geologic matrix. (It is also, however, the redox condition amenable to Iron Related Bacteria, a common and prolific subsurface bacteria that can clog wells with bioslime and accumulated biomass if sufficient nutrients are available to support biometabolism).
- The variability of electrical conductivity (EC) in the MCWP-MW03 samples indicates that water in this well is likely being influenced by tidal action. This finding is in practicality non-sequitur with respect to the modeling simulations, as the precipitation potential of compounds is not significantly influenced; however, it is an indication of hydraulic connectivity between the CCG aquifer and the Pacific Ocean.
- Saturation conditions (i.e. the mineral saturation, under-saturation, or oversaturation of the waters) were evaluated for all components. In general, all of the waters showed near-equilibrium saturation conditions (i.e., Saturation Index (SI) values between -1.0 and +1.0 with the exception of SI's for Gibbsite ($Al(OH)3$), an Aluminum oxide compound). Because the model did not include the chelating effects of organic carbon compounds, the results should be considered overly conservative, and with these equilibrium values having been calculated for the native waters themselves, there is likely such a chelating effect taking place, or a slight metastability condition that precludes precipitation of Aluminum hydroxides. This SI condition was taken into account in the Step 3 mixing modeling.
- Other than noted above, there was no indication of scaling potential from iron, calcium, or silica related compounds.

3 – Simulation of Mixing and Displacement of the Injection Waters

Mixing and displacement of the injection waters upon introduction to the aquifer was simulated with the purpose of evaluating the equilibrium state of the resulting mixes. The results of our evaluation are presented below:

- Mixing of the waters was modeled using a variety of NGW/injectate ratios, with the water qualities taken from the lab analyses, and with the minor but realistic assumption that the injected recycled water will have a free Chlorine Residual of 1.0 mg/L and a measurable dissolved oxygen (DO) level (assumed at 0.45 mg/L) accounting for the passage through the proposed CCWTF.
- The NGW/injectate mixing ratios were also subjected to equalization with the mineral matrix of the CCG aquifer lab results.
- The mixing simulations used the baseline SI's of the natural conditions (i.e., those established in Step 2 above) as the practical threshold of oversaturation/precipitation of the mixture. This assumption is both common and realistic based on the unique conditions found in every aquifer that cannot be replicated in a single equilibrium database such as the LLNL compilation.
- The mixing model results show a slight oversaturation and precipitation potential for iron-related and aluminum-related oxides, although the modeled amounts of precipitation are relatively low for MCWP-MW01 and -MW02 (less than 1 mg/L). These values could be metastable and/or chelated by organic carbon enough to have no precipitation potential whatsoever. Field injection trials with representative recycled source water would confirm this potential.
- The precipitation potential for MW-03 is slightly higher than MW-01 and MW-02, however, it is still below 1 mg/L, and not considered problematic.

In summary, the modeling suggests that the potential for precipitation/scaling due to the injection of the proxy-simulated injection water is minimal, and at a theoretical maximum would be at such small levels to be non-problematic for ongoing operations.

BIOFOULING ISSUES

The potential for biofouling in injection wells is always present, as the presence of subsurface aquatic biota is ubiquitous in the environment, and in most cases, the injected water is different in some way from the native ground water. There are some basic elemental building blocks necessary for living organisms; these include the compounds of carbon, oxygen, nitrogen, and phosphorous (C, O, N, and P). The presence of these components, often referred to in environmental geochemistry as "nutrient compounds," provide the ability of subsurface biota to proliferate as long as the ratio of nutrients and the aqueous redox environment is suitable to allow metabolism of the food (nutrient) supply. It is typical in the aqueous subsurface environment for phosphorous to be the most "limiting" compound to unlimited biogrowth, as it is both essential to bioactivity and rare in the environment. The second most limiting compounds in subsurface bioactivity are nitrogen compounds. It is common to refer to these environments as "P-limited" or "N-limited", because the only issue that prevents unlimited biogrowth is the lack of these essential nutrient compounds. Most natural aquifers are P- and/or N-limited.

The evaluation of nutrient supply and supportive metabolism environment were evaluated for the proposed project, and the following findings were noted:

- The proposed injection water likely has adequate levels of N, P, and C to support ongoing biometabolism in the aquifer.
- Because of the method of direct injection via wells, biometabolism would be greatest near the well screens as this is the origin of the nutrient supply.
- The addition of the treated effluent alters the subsurface such that neither N nor P compounds will be limitations on food supply, thus allowing proliferation of an opportunistic biota.
- Based on the composition and ratios of nutrients in the injectate, the only means of controlling biofouling would be if the organic carbon present in the injectate was completely destroyed via oxidation or other means to render it unavailable for biometabolism. (The other method to control bioactivity not mentioned is to limit the P and N levels in the injectate via enhanced treatment processes at the CCWTF.)
- The equilibrium modeling results showing the Fe(2+)/Fe(3+) redox condition indicate that biofouling would likely be comprised of iron-related bacteria (predominantly) which, although non-pathogenic in nature, is a virulent genre of biofoulants characterized by a high biomass, slime-forming nature that is particularly problematic with respect to the plugging of wells.
- The modeling indicates that based on nutrient supply, the most problematic periods of operation would be when the wells are dominated by the injection water, i.e. fouling would be greatest when injection operations were occurring.

We hope the above discussion assists in the understanding of the attached geochemical analysis report. Please give let us know if you have any questions or require additional information.

ATTACHMENT A – GEOCHEMICAL ASSESSMENT REPORT

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F: 61 2 4227 5154
www.ecoengineers.com
ABN 74 078 666 510

25 November 2013

Robert Marks
Principal Hydrogeologist
Pueblo Water Resources Inc.
4478 Market Street, Suite 705
VENTURA CA 93003

Basic Geochemical Review and PHREEQC Modeling to Provide Initial Assessments of Issues Associated with the Proposed Malibu Aquifer Injection Treated Effluent Sub-surface Disposal Scheme (Malibu Centralized Waste Water Project).

Dear Robert

Thank you for engaging Ecoengineers Pty Pty Ltd (‘Ecoengineers’) to conduct an initial geochemical assessment of the principal issues associated with this proposed sub-surface treated wastewater disposal scheme based on our professional experience and underpinned by PHREEQC model-based assessment of core chemistries, the identification of mineral equilibrium saturation levels and their attendant influence on potential precipitation and scaling effects under a treated wastewater injection/storage scenario as well as some preliminary assessment of the potential for well biofouling during injection.

Background Information

It is important to note that our assessment was made using verbal advices from Pueblo Water Resources (‘PWR’) and the following data deliverables supplied to us:

1. Field water quality monitoring data for an approximate proxy of the likely Injectate water (being a chlorine-treated effluent), identified as “Lumberyard” and three injection wells designated MW-01, MW-02 and MW-03 being, temperature, pH, Specific Conductance (= Electrical Conductivity; EC; corrected to 25 C), a field Redox Potential denoted ‘ORP’ being a potential relative to a Ag/AgCl reference electrode with 4.0 M KCl filling solution (electrolyte) at the water temperature, Chlorine Residual (mg/L as Cl_2) and Dissolved Oxygen (DO; mg/L). These data were obtained on 10 September, 6 August, 29 August and 8 July 2013 respectively (only).
2. Detailed, individual laboratory analysis reports on the Lumber Yard waste water treatment plant water and the groundwaters sampled from the three wells MW-01, MW-02 and MW-03 on the above dates (only) issued by the Eurofins Eaton Analytical (Monrovia, CA) laboratory. It is noted that a wide suite of parameters were reported-on by this laboratory, including both filterable and total (unfiltered) values for numerous parameters as well as Disinfection By-Products (DBPs).
3. A copy of a master spreadsheet from the Lumber Yard Plant containing the records of chemical monitoring of the Plant Effluent during 2012.
4. A copy of the report: RMC Water and Environment (2012) Technical Memorandum: Conceptual Groundwater Injection Plan. June 2012 (prepared by: Steve Clary, RMC

Water and Environment, Dan Wendell, Groundwater Dynamics, Richard Laton, Earth Forensics and Daniel J. Morrisey, McDonald Morissey Associates, Inc.)

5. Two bacterial assessment reports #19579 and #19615 by Water Systems Engineering Inc., of Ottawa, Kansas, being respectively one for a sample from proposed injection well MW-01 sampled on 6 August 2013 and one for a sample of the Lumber Yard Plant Effluent taken on 10 September
6. Detailed mineralogical analysis reports for grab sample aquifer lithological material recovered previously during the drilling of each of these three wells in February 2012 issued by Mineralogy, Inc. of Tulsa, Oklahoma. It is noted these reports included XRD, XRF, and Cation Exchange Capacity data and also detailed lithological descriptions and classification information. The latter described the aquifer materials as unconsolidated and disaggregated feldspathic, litharenitic sands. They also included references to the common presence of ironstone and Fe oxides possibly representing altered and recrystallized volcanic rock fragments at all three locations. It is notable from the descriptions of all three samples of lithic material recovered during drilling that they were all devoid of authigenic carbonate or sulfate overgrowths, intergranular cements or fracture infill materials, nor were there visible signs of siliceous e.g. chalcedony overgrowth or infill. Useful estimates of the ranges of void porosity were also given, albeit qualified by a potential for clay migration and/or swelling effects associated with the dominant montmorillonite clay – which XRD showed was typically present at around 13 – 17% by weight.

Assessment

In making our assessment we first critically reviewed all field and laboratory data in accord with best practice, especially in respect of data quality.

Laboratory Data Review

We conducted a comprehensive review of the 7 water quality reports from the Eurofins Eaton Analytical Monrovia laboratory. We found these reports to be of a generally adequate quality but there were some significant issues we identified for which an explanation could not be found, as follows:

1. The laboratory reports for the Lumber Yard effluent and for wells MW-02 and MW-03 were split into two sets, being one for the filtered samples indicating essentially the true solution concentrations and one for the unfiltered samples indicating the included colloidal material. However in the case of well MW-01 there was only one report which included the reporting of both filtered and unfiltered data, often on the same page. Consecutive pages in that report contained mixtures of filtered and unfiltered data which could lead to confusion unless very carefully read.
2. There were inexplicable shifts in Method Detection Limits (MDL) and Method Resolution Limits (MRL), particularly in the MW-01 report. For example, the Total Filtered Aluminum MDL and MRL (by ICP method) were quoted as 0.23 and 0.50 mg/L respectively versus ranges of 0.046 - 0.12 and 0.10 – 0.25 (also by ICP) in all other reports. The explanation given was coded D1 - Sample required dilution due to matrix. Such an explanation is at odds with the fact that all other waters sampled had comparable or sometimes significantly higher salinity e.g. the MW-03 sample. In addition, the NO_3-N (by EPA 300.0 method) MRL was quoted as 0.5 mg/L for the MW-01 water report whereas it was given as 0.25 for NO2-N in the same report and also typically given as lying in the range 0.12 - 0.13 mg/L for all the other samples (for the same method).
3. Most importantly, the single laboratory report for the Lumber Yard Effluent reported, for the nutrients; (nitrate nitrogen) NO_3-N = 0 mg/L, (nitrite nitrogen) NO_2-N = 0 mg/L, (Total Kjeldahl Nitrogen) TKN = 0.66 mg/L, (ammonia nitrogen) NH_3-N = 0.019 mg/L, (total nitrogen) TN = 0.68 mg/L, (phosphate phosphorus) PO_4-P = 1.0

mg/L and (total phosphorus) TP = 0.98 mg/L. These data compare most unfavourably with the data found in the internal Plant master spread sheet for the entire year of 2012 supplied by PWR which shows the following mean values for these parameters ± one standard deviation with the total number of measurements (n) which led to those values; NO_3-N = 0.64±0.07 (n = 52), NO_2-N = 0 (n = 52), TKN = 0.35±0.05 (n = 52), NH_3-N = 0.33±0.05 mg/L (n = 52), TN = 0.99±0.08 mg/L and TP = 0.51±0.16 mg/L (n = 12). The comparison suggests that *either* the Eurofins laboratory has analytical problems for the NO_3-N and TKN methods or, *alternatively* there were plant operations or sampling issues applying with the sample taken on 10 September 2013.

We also conducted a comprehensive review of the extensive mineralogical report by Mineralogy Inc., of Tulsa. We found that report to be a model of clarity and careful presentation and we could find no significant quality issues with it.

We also reviewed the two small reports bacterial assessment reports by Water Systems Engineering ('WSE') and could find no significant quality issues with them.

It is noted that basic chemical parameters (pH, TDS, Electrical Conductivity. Oxidation Reduction Potential (ORP) chlorine (unusually expressed as Cl not Cl_2, and Iron (resuspended) were also reported by WSE.

Interestingly, these (WSE) chemical parameters seem to have been measured upon receipt at the Water Systems Engineering laboratory as they differ significantly from e.g. the field data reported by PWR (see below). We have not been briefed on whether best practice protocols such as chilling, collection with zero headspace etc., transportation chilled etc., applied to these samples.

Field Data Review

We tabulate below in **Table 1** the field data as supplied by yourself but correcting the observed field redox potentials to an Eh (true ORP) relative to the standard hydrogen electrode (SHE) at the observed temperature. The ECs are reported normalized to 25 C as is usual. NA = data Not Available and ND = Not Detected.

Table 1: Field Water Quality Parameters

Site ID	Date	pH	EC (µS/cm) (25 C)	Temp. C	Eh (mV)	Cl_2 (mg/L)	DO (mg/L)
Lumber Yard Effluent	9/10/13	7.6	1373	28.4	+144 (WSE +186)	0.02 (WSE 0.015)	4.9
MW-01	8/6/13	7.3	2070	20.5	+119 (WSE +213)	0.00 (WSE ND)	0.0
MW-02	8/29/13	7.6	2100	21.2	+18	0.00	0.1
MW-03	7/8/13	7.3	2560	22.3	+231	NA	NA

Initially, we modeled the geochemistry of these four waters using USGS PHREEQC version 2.18 and the USGS default database (phreeqc.dat) dated 1 October 2010 and subsequently where required the Lawrence Livermore National Laboratory database (llnl.dat) dated 9 February 2010 version recently distributed with PHREEQC version 3 which is the most recent, most comprehensive and up to date database.

The following **Table 2** compares our model-predicted ECs (@ 25 C) with the PWR field measured values and the WSE laboratory values.

Table 2: Model-estimated ECs versus Field ECs

Site ID	Date	PWR Field EC (µS/cm) (25 C)	WSE Lab EC (µS/cm) (25 C)	PHREEQC model-estimated EC (µS/cm) (25 C)
Lumber Yard Effluent	9/10/13	1373	1425	1402
MW-01	8/6/13	2070	1860	2225
MW-02	8/29/13	2100	NA	2221
MW-03	7/8/13	2560	NA	3343

All field measured EC values agreed well with the PHREEQC estimated values with the exception of well MW-03. Matching of the PHREEQC estimated EC with the observed EC would have required a reduction in NaCl concentration of at least 60 percent (from 650 mg/L to at least 260 mg/L).

Upon discussions with yourself you advised that a previous 14-hr pumping test performed on well MW-03 in 2011 had indicated EC values during that test ranging between 3040 and 3760 uS/cm, averaging 3650 uS/cm – a value very similar to what our PHREEQC model suggests. Interestingly, the EC during that pump test had started out at the low end of the range and steadily increased for about 6 hours, after which it stabilized at around 3700 uS for about 7 hours, but then began to decline again during the last hour before the test was shut down.

This suggested a possible tidal influence on the salinity in well MW-03 (i.e., the seawater/freshwater interface could be rising and falling as the tide rises and falls twice per day). Unfortunately, what was planned to be a 72-hour test was shut down after only 14 hours due to logistical and/or budgetary constraints.

Nevertheless, these observations provides a plausible explanation for why there is a discrepancy between the field EC measured (at 12:30 hours on 7/8/13) and that predicted by PHREEQC for the actually water chemistry as reported by the Eurofins Eaton Analytical Monrovia laboratory (for all significant cations and anions).

These observations (in July 2013 and in 2011) do suggest that the well perforated intervals of at least well MW-03 falls somewhat within the sphere of influence of the local saline/freshwater interface and this then also raises the relevant question as to whether this phenomenon would also affect wells MW-01 and MW-02 (or indeed any others which may be installed for this Project).

As Eh is so important to geochemistry, particularly when mixing waters of different type containing redox sensitive elements such as iron (Fe), manganese (Mn), ammonia nitrogen (NH_3-N), nitrite/nitrate nitrogen NO_x-N), dissolved organic nitrogen (Org-N), arsenic (As), selenium (Se), uranium (U) etc., as in this Project, we also established PHREEQC model redox potentials for the most common redox couples which may apply in these waters especially if bacterial action is occurring, and/or reduced carbon such as methane etc., DO and/or Cl_2 are present. These are the:

- ferrous/ferric couple i.e. Fe(+2)/Fe(+3);
- ammonia/nitrate couple i.e. N(-3)/N(+5); :
- dissolved oxygen/water couple i.e. O(-2)/O(0) in the case of the Lumber Yard effluent;
- chloride/hypochlorite (aqueous chlorine) couple i.e. Cl(-1)/Cl(+1)

These model-predicted potentials were compared with the measured Ehs to determine which couple was likely to be dominating the observed Eh (redox status) of the water in reality. In the case of the ferrous/ferric couple i.e. Fe(+2)/Fe(+3) we assumed that the filterable Fe was all Fe(+2) and that the insoluble Fe as indicated by the difference between the filtered and total analyses reported by Eurofins was all colloidal ferric hydroxide $Fe(OH)_3$ i.e. in the Fe(+3) oxidation state.

Experience shows this is usually a reasonable approximation which allows determination of the dominant redox couple applying. In some cases; if a parameter concentration was quoted in the lab report as less than the Method Detection Limit (MDL) we assumed as usual that the parameter was present at a concentration of half of the MDL.

The following **Table 3** shows the proximity of the redox couple closest to the observed Eh. NA = Not Applicable where the groundwaters have of course not been subject to chlorination.

The outcomes were predictable and plausible for all waters as it is well known that the reduction of sulfate occurs in the Eh region – 200 to +100 mV, the (abiotic or biotic) reduction of Fe occurs in the region +180 to +400 mV, the reduction of Mn occurs in the region +220 to +500 mV and the (biotic) reduction of nitrate/nitrite in the region +300 to +600 mV.

Table 3: Observed Field Eh versus Model-Estimated Redox Couples

Site ID	**Observed Field Eh (mV) by PWR**	**Observed lab. Eh (mV) by WSE lab.**	**Model-predicted Fe(+2)/Fe(+3) couple potential (mV)**	**Model-predicted N(-3)/N(+5) couple potential (mV)**	**Model-predicted O(-2)/O(0) couple potential (mV)**	**Model-predicted Cl(-1)/Cl(+10 potential (mV)**
Lumber Yard Effluent	+144	+186	+124	+316	+740	+1196
MW-01	+119	+213	+256	+370	NA	NA
MW-02	+18	NA	+231	+325	+743	NA
MW-03	+231	NA	+225	+340	NA	NA

More specifically, this exercise showed that; on this occasion the very low Chlorine Residual field measurement for the Lumber Yard water is probably in error and there was in reality no residual chlorine present on the water at the time of monitoring, resulting in the Eh being dictated by the common natural Fe(+2)/Fe(+3) couple.

The Effluent field Eh value of +144 mV was validated by the similar WSE lab value of +186 mV and is just not compatible with the presence of a strong oxidant such as chlorine (or hypochlorite). It is also theoretically well below the redox potential which might be imposed by the relatively high DO value of 4.9 mg/L (which implies a O(-2)/O(0) couple redox potential of around 750 mV) but this latter value might simply be a function of slow oxidation kinetics with a chemically complex dissolved organic carbon (DOC; which was quite high at 6.1 mg/L) and the absence of reactive reduced carbon species such as low MW organic acids etc.

The outcomes were predictable and uniformly the same for all the native groundwaters (NGWs) in that the observed Ehs were probably all largely dictated by the common natural Fe(+2)/Fe(+3) couple and this is their likely usual state in the absence of injection of another water containing strong oxidants or reductants. This finding accords well with the mineralogical examination by Mineralogy, Inc., which indicated the common presence of ironstone and Fe oxides possibly representing altered and recrystallized volcanic rock fragments at all three locations, indicating an ample supply of oxidized ferric material.

PHREEQC Modeling Outcomes and their Interpretation

Initially we modeled these actual waters individually to better understand their salinities, the analytical quality of their cation/anion balances and the salient features of their overall actual geochemistry. Please note that in the following text we sometimes refer to the waters sampled from wells MW-01, MW-02 and MW-03 at being NGWs (Natural Ground waters) as opposed to the 'Injectate', which refers to the treated Lumber Yard plant effluent or a simulated future proxy Injectate comprised of a treated waste water based on the observed Lumber Yard Effluent chemistry but modified, as advised by you to probably have a Chlorine Residual of 1.0 mg/L (as Cl_2) and a DO of say around 0.45 mg/L as O_2.

The actual PHREEQC geochemical input files (.phrq extension) and output files (.out extension) of the as-sampled Lumber Yard Effluent and of the three NGWs are appended to this report. These output files were obtained by modeling using the llnl.dat database. They may be inspected with any text file viewer such as Notepad or Wordpad. The following **Table 4** lists the calculated cation/anion balances and the Saturation Indices (SIs) of the most common scaling minerals i.e. Barite (barium sulfate), Calcite (calcium carbonate), Chalcedony (Opaline silica), Gibbsite (aluminium hydroxide) and $Fe(OH)_3$ (hydrous ferric oxide).

Note these outcomes do not take into account the effect of any organic complexation which may be applying to relevant Ba, Ca, Mg, Al or Fe etc., aqueous species *so the SIs should be considered maximal, ie these outcomes are conservative in their estimation of scaling potential*.

In general, a positive SI, particularly greater than about +1.0 indicates a significant potential for scaling/precipitation whereas a lower or negative SI implies negligible or no such potential. In **Table 4** we have also recorded the (base 10) logarithms of the partial pressures of CO_2 which,-via equilibrium with aqueous CO_2 and bicarbonate - is responsible for producing the observed field pHs. The effective partial pressures of CO_2 (pCO_2) in any gas phase in equilibrium with these waters may be easily determined by taking the antilogarithm of the these values e.g. antilog -2.00 gives 0.01 or 1.0% CO_2 (by volume).

Further details of these modeling techniques may be found in Ecoengineers Pty Ltd (2008).

Table 4: Analysis cation/anion Balances and Principal Mineral Saturation Indices

Site ID	Cation/ Anion Balance (%)	Barite SI	Calcite SI	Chalcedony SI	Gibbsite SI	$Fe(OH)_3$ SI	Log pCO2
Lumber Yard Effluent	+1.27	-1.05	-0.10	+0.03	+1.96	-1.14	-2.25 (i.e. pCO_2 =0.56%)
MW-01	+2.64	+0.60	+0.32	+0.60	+1.78	-0.63	-1.88 (i.e. pCO_2 = 1.32%)
MW-02	+0.46	+0.64	+0.66	+0.57	+0.49	+0.58	-2.11 (i.e. pCO2 = 0.78%)
MW-03	+5.05	+0.89	+0.78	+0.64	+1.69	-0.30	-1.56 (i.e. pCO2 = 2.75%)

Cation/anion balances were acceptable in all instances except for the NGW MW-03 where it was just outside the normal accepted limit of ±5.0%. This indicates the cation inventory contains an erroneous high cation concentration value or the anion inventory an erroneously low anion concentration value. Noting the issues with reconciliation of the field and theoretical ECs (see **Table 2** above) this discrepancy mostly likely concerns erroneously high Na or erroneously low sulfate, alkalinity or chloride analyses involving separate sample bottles taken at slightly different times.

Nevertheless, these model outcomes for the Lumber Yard Effluent and NGWs suggest that; upon mixing the Lumberyard Effluent with these NGWs there is unlikely to be significant calcareous or siliceous scaling issues arising in the injection wells.

There are however indications of possible aluminous scaling or precipitation and, noting that as a real Injectate chlorinated to a standard chlorine residual of say ~1.0 mg/L would be much more oxidizing (much higher Eh) than the actual sampled Lumber Yard Effluent which had a much lower chlorine residual and hence a much lower Eh, such that there may also be some more $Fe(OH)_3$ precipitation than indicated by the above SIs.

We therefore next established slightly more complex PHREEQC Effluent/NGW mixing and aquifer storage models in which we assumed that:

1. a fully chlorinated Injectate with a composition equivalent to the Lumber Yard Effluent but with a chlorine (Cl_2) residual of 1.0 mg/L and a DO of 0.45 mg/L as suggested by yourself was injected into each of the MW-01, MW-02 and MW-03 wells; and
2. in each case, mixing at ratios of 25% : 75%, then 50% : 50% and then 75% : 25% of Injectate : NGW respectively was simulated; while at the same time
3. the mixture comes to full cation exchange (‘catex’) equilibrium with the Ca, Mg, Na and K major cations on the lithology in these aquifers as determined by Mineralogy Inc., and at the same time
4. coming to full CO_2 solubility equilibrium with the partial pressure dictated by the previous modeling applying in that part of the aquifer as shown in the above table; but at the same time
5. not precipitating any minerals *unless their SIs exceeded those which had been previously observed in that particular NGW at that particular partial pressure of* CO_2 on the grounds that; the observed NGW mineralogies reported by Mineralogy Inc., clearly showed no precipitation/overgrowth/infill of Ba (sulfate), Sr, Ca, Mg (carbonate) or SiO_2 minerals and only precipitated Fe oxyhydroxides (hydrous oxides).

It is noted in condition 3 above that the size of the catex suite of exchangeable cations applying per litre of the various mixtures listed in item 2 is a modeled function of the amount of each exchangeable cation on the solids (meq/100g) as measured by Mineralogy Inc., multiplied by the estimated total mass of those solids in contact with each litre of water.

Thus the calculation of each suite requires taking into account the estimated porosity of the aquifer in each well (as estimated by Mineralogy, Inc., from their thin section analysis) and the particle density of the solids which is assumed as usual to be 2.65. For example; the solids from MW-01 had 8.13 meq/100 g solids upon which calcium (Ca) is occupying catex sites.

For a lithology which has an average porosity of around 37.5% as suggested, this means that every litre of water is exposed-to a total solids volume of 1/0.375 – 1.0 = 1.667 litres of solids or some 1.667 x 2.65 = 4.417 kg of solids for a total of 44.17 x 8.13 x 0.001 = 0.3591 eq/L Ca-occupied catex sites ($Ca_{0.5}X$) or 0.1796 moles/L CaX_2 catex sites. A useful way of converting from units of meq/100g to units of meq/L is to note that:

- 1 meq/100g = (10.ρ/n) meq/L where ρ = dry bulk density (= 0.625 x 2.65 = 1.656) and n= porosity (0.375) giving a conversion factor of 10.1.656/0.375 = 44.17

The PHREEQC llnl.dat database includes typical clay minerals (especially appropriate to smectites like montmorillonite) exchange constants for Na, K, Ca, etc., Mg exchanging on those sites (including barium Ba and strontium Sr etc.).

The mineral solubilities we assessed in this manner with respect to possible precipitation/scaling (by assuming equilibrated Injectate/NGW mixture SIs would then exceed that previously established in the respective NGW) were:

Barite [$BaSO_4$]
Calcite [$CaCO_3$]
Disordered Dolomite [CaMg(CO3)2]
Celestite [SrSO4]
Chalcedony [opaline SiO2]
Dawsonite [NaAlCO39OH)2]
Hydrous Ferric Oxide [Fe(OH)3]
Gibbsite [Hydrous Aluminium Oxide; $Al(OH)_3$]
Magnesite [MgCO3]
Rhodochrosite [MnCO3]
Strontianite [SrCO3] and
Witherite [BaCO3].

The following **Table 5** identifies the major minerals which may cause scaling or precipitation during the injection of a proposed Injectate with the chemical composition of the Lumber Yard Effluent but with a chlorine residual of ~1.0 mg/L and a DO of ~0.45 mg/L, but accords NIL potential for scaling/precipitation if the computed SI does not exceed that observed in the respective NGW.

Once again it is noted that the prediction is conservative because the model neglects the effect of any additional organic complexation effects, particularly of Fe and Al due to dissolved organics present in the Injectate.

Table 5: PHREEQC model-predicted precipitation of Minerals upon Mixing of Injectate and NGWs in wells MW-01, MW-02 and MW-03.

Proxy Injectate (vol. %)	NGW (vol. %)	NGW type	Mass of Barite possibly formed (µg per litre of mixture)	Mass of Calcite possibly formed (µg per litre of mixture)	Mass of Chalcedony possibly formed (µg per litre of mixture)	Mass of $Fe(OH)_3$ (Hydrous Ferric Oxide) possibly formed (µg per litre of mixture)	Mass of $Al(OH)_3$ (Gibbsite) possibly formed (µg per litre of mixture)
25	75	MW-01	NIL	NIL	NIL	7.0	59
50	50	MW-01	NIL	NIL	NIL	7.2	120
75	25	MW-01	NIL	NIL	NIL	6.6	180
25	75	MW-02	NIL	NIL	NIL	8.0	NIL
50	50	MW-02	NIL	NIL	NIL	NIL	31
75	25	MW-02	NIL	NIL	NIL	NIL	104
25	75	MW-03	NIL	NIL	NIL	40	NIL
50	50	MW-03	NIL	NIL	NIL	26	140
75	25	MW-03	NIL	NIL	NIL	10	213

Biofouling

In assessing the likelihood of biofouling deposits, especially during aquifer injection and storage we note that the most important controlling factors for biofouling of injection well screens and within the aquifer adjacent to injection wells are as follows:

1. Are there are adequate levels of nitrogen and phosphorus nutrients to sustain the bacterial action? These nutrients allow growth of significant biofilm mass being a mixture of bacteria and exuded extracellular material (largely polysaccharide ‘gel’). Very often there is an adequate supply of nitrogen nutrients (nitrate, ammonia, etc.) but insufficient phosphorus in which phosphorus – especially phosphate - becomes the limiting nutrient. In that case the system is described as P-limited. These processes can be modeled with PHREEQC when adequate information is available. That situation does not apply in the present preliminary assessment stage.
2. Are there adequate levels of soluble and/or total organic carbon (DOC or TOC) to support growth of a bacterial biomass?
3. Has a disinfectant technique such as chlorine, hypochlorite, hydrogen peroxide, ozone or UV irradiation capable of destroying (by oxidation), been used in the Injectate?

The single Lumber Yard (proxy) Effluent sample analysis (by Eurofins) did not have TN level significantly higher than was observed in the three NGW (only a Total Kjeldahl Nitrogen (TKN) of 0.66 mg/L, with ostensibly no ammonia (NH_3) or nitrate/nitrite NOx) but a significantly higher TP level (~1.0 mg/L).

If this was a true proxy for the final treatment plant for the Project this would have meant that the Lumber Yard Effluent could only contribute organic nitrogen to the native groundwater/Injectate mix and hence with an Injectate of that nature the nitrogen supply would be the biofouling-limiting nutrient. This in turn would suggest that phosphorus would not be the limiting nutrient in the Injectate.

However, as discussed above, we found strong evidence that the single Lumber Yard (proxy) Effluent sample analysis (by Eurofins) either had significant errors with respect to nitrogen (N) nutrients or that there were Plant operational or sampling issues on the date of sampling which adversely changed nutriment levels away from the long term means and likely ranges. For this reason, we do not consider this a likely conclusion for a real world Injectate as most secondary and tertiary treated effluents contain significant concentrations of nitrate and ammonia.

The inhouse Plant record for 2012 for the Lumber Yard Plant showed that the TN in the Plant Effluent over 2012 was 0.99±0.08 mg/L (n = 52) and the TP was 0.51±0.16 mg/L. This gives a TN/TP mass ratio of the order of 2. This is a condition of *no phosphorus limitation* as bacterial biomass has a typical stoichiometric N/P mole ratio of around 4 – 6 equivalent to a mass ratio of around 1.8 – 2.7.

It is also noted that the June 2012 RMC Water and Environment technical memorandum suggests a TN (= TKN + NO_3-N) of around 11 + 6.5 = 17.5 and a PO_4-P of 3.0 mg/L. The N/P mass ratio of that effluent would be 2.6, *again a condition of no phosphorus limitation.*

At this preliminary assessment stage it was considered likely the Injectate would be chlorinated, especially if there was any possible intention to subsequently re-extract water from the aquifer and re-use it e.g. for irrigation.

In our PHREEQC modeling of the scaling/precipitation propensity we therefore assumed that:

1. the residual Dissolved Organic Carbon (DOC) in the Injectate has been completely destroyed by oxidation using one the above disinfection techniques i.e. Injectate organic carbon has been completely deactivated or destroyed and cannot support biomass production; and

2. a suggested chlorine residual of ~1.0 mg/L (as Cl_2) invariably applies to the Injectate; and
3. the Injectate contains 0.64 mg/L NO_3-N and 0.33 mg/L NH_3-N as indicated by the Lumber Yard Plant data spreadsheet for 2012; and
4. the NGWs still have, prior to mixing with Injectate, the levels of DOC reported by the Eurofins laboratory.

The following **Table 6** tabulates the Eh potentials of the inground mixtures and the estimated residual levels of C(-4) i.e. reduced, organic carbon (DOC) in the Injectate/NGW mixtures.

Table 6: Effect of Injecting an Injectate with no bioavailable carbon but a 1.0 mg/L Chlorine Residual

Proxy Injectate (vol. %)	NGW (vol. %)	NGW type	Predicted Eh of mixture (mV)	Mixture minimum DOC (mg/L)	Mixture minimum NO_x-N (mg/L)	Mixture minimum NH_4-N (mg/L)
25	75	MW-01	-186	0.62	NIL	0.008
50	50	MW-01	-184	0.27	NIL	0.006
75	25	MW-01	+673	NIL	0.017	NIL
25	75	MW-02	+671	NIL	0.032	NIL
50	50	MW-02	+677	NIL	0.056	NIL
75	25	MW-02	+750	NIL	0.061	NIL
25	75	MW-03	+690	NIL	0.020	NIL
50	50	MW-03	+767	NIL	0.042	NIL
75	25	MW-03	+776	NIL	0.054	NIL

As can be seen, as the components required for biomass production are all minimal in the above **Table 6** and rely on the assumption of N-nutrient and DOC contributions by the Injectate, the assumption that the Injectate does not contribute DO, N-nutrients or ‘feedstock’ DOC into the Injection Zone is a critical one.

The period of highest risk for biofouling would therefore occur when the proportion of stored water in the aquifer is dominated by Injectate i.e. when greatest concentrations of TP and NO_x-N apply.

This can only be controlled by control of the concentration of residual DOC after disinfection and immediately before injection.

Unfortunately, at present we do not have, in the Lumber Yard Effluent, a sufficiently accurate proxy to indicate what the real ‘advanced Plant’ Injectate DOC, TN and TP composition would be, nor even confirmation as to whether TN levels would be significantly higher in the Injectate than in typical NGWs as the RMC June 2012 technical memorandum strongly suggests.

It is therefore premature to attempt to model the potential biological situation any further.

Summary of Assessment

The major findings of this preliminary assessment of geochemical issues of the Proposed Malibu Aquifer Injection Treated Effluent Sub-surface Disposal Scheme are as follows:

Any Injectate would clearly be aerobic and contain at least some dissolved oxygen if not other oxidants such as chlorine or peroxide etc. There are adequate levels of reactive dissolved organic carbon (DOC) in the aquifer to ensure that the already relatively high partial pressures of CO_2 in the aquifer (0.8 – 2.8%) would only increase upon injection/mixing, increasing the solubility of carbonates still further. The potential for abiotic (i.e. without biological influence) calcareous precipitation/scaling is very low.

The native groundwater geochemistry is just anoxic rather than fully aerobic i.e. reduction of sulfate or organic matter is clearly not occurring naturally as deduced from the absence of dissolved methane and sulfide but a low level of reduction of iron is probably occurring as indicated by chemical analyses and redox potential (Eh) measurements.

Any precipitation in the zone of injection is only likely to involve precipitation of small amounts of aluminum and iron hydrous oxides (oxyhydroxides). Such aluminum and iron hydrous oxide precipitates are usually not problematic unless associated with biofouling as follows.

Due to the relatively high total or dissolved organic carbon (TOC; DOC) level in the NGWs (ranging from 1 – 6 mg/L depending upon location), the relatively high level in the Lumber Yard proxy Effluent (>6 mg/L), as well as the suggested magnitude of supply of DOC in the June 2012 RMC Water and Environment technical memorandum (9.5 mg/L), and the likely lack of phosphorus limitation, we conclude the potential for biofouling of injection wells screens and within the aquifer storage area is relatively high. unless it can be shown that chlorine or some other oxidizing disinfectant has largely destroyed the TOC and/or DOC in the actual treatment plant effluent proposed for an Injectate to the local aquifer.

Unfortunately, on chemical grounds, both the Lumber Yard Effluent field and laboratory analyses and the numbers given in the June 2012 RMC Water and Environment technical memorandum do not tell us anything particularly reliable about these parameters in the Treatment Plant Effluent Injectate created for the Scheme.

The Lumber Yard Effluent analysis did however show significantly high TP levels (~1.0 mg/L), and the June 2012 RMC Water and Environment technical memorandum suggested a likely PO_4-P level of around 3.0 mg/L.

At least we can say with some confidence that such levels both indicate that the zone of injection would not be subject to any phosphorus (P) limitations on biofouling.

But as noted above, at present we do not have a satisfactory proxy to indicate whether TN levels would be significantly higher in the Injectate than in the NGW nor what the likely N-nutrient speciation pattern would actually be. Thus we are unable to conduct model simulations of biofouling potential with any confidence.

It is noted the N-species values quoted in the June 2012 RMC Water and Environment technical memorandum contain a mathematical error in that the predicted ammonia nitrogen (NH_3-N) level of 13.3 mg/L exceeds the predicted Total Kjeldhal Nitrogen (TKN) level of 11.0 mg/L which is strictly impossible as TKN = NH_3-N + Org-N.

The PHREEQC predictions of likely low level Fe and Al oxyhydroxide precipitation upon mixing of Injectate and NGWs and the observed mineralogical occurrence of secondary Fe oxides in the aquifer mineralogy (refer Mineralogy Inc. report) suggests that biofouling would most likely be comprised of deposited Fe oxyhydroxides and biomass comprising Fe-reducing bacteria and their associated extracellular slimes.

In our view, at this stage, the fact that the Fe/Mn oxidizing bacteria were not detected by the Water Systems Engineering laboratory bacterial studies in either the Lumber Yard Effluent or in a sample of the MW-01 NGW is not particularly relevant to this conclusion.

The above key findings are obviously important from an injection, performance, capacity, and maintenance perspective (i.e. injection well operation and maintenance issues).

In addition to the potential for Fe- and Al-based precipitation/scaling and/or biofouling, however, another issue particularly important to regulators is the potential for dissolution/mobilization of metals or other elements or chemical of concern. Below is an excerpt from the Findings of a recently adopted ASR general permit in California related to this issue:

Finding 28. Finally, injection of water into any aquifer may induce geochemical reactions, some of which may cause exceedance of a water quality objective. For example, the introduction of water with a higher concentration of dissolved oxygen into an anaerobic aquifer may induce geochemical oxidation-reduction (or "redox") reactions that increase concentrations of inorganic species in the aquifer and recovered water. The redox reactions may result in higher dissolved concentrations of inorganic constituents in recovered water than in the injected water. Specifically, arsenic, iron, manganese, nitrogen, selenium, and sulfur have been identified as constituents of concern in ASR projects.

If this project does not propose to recover injected water for any possible reuses then it may be concluded that Finding 28 does not really apply. This would appear to be a regulatory issue requiring clarification.

If there were possible reuses contemplated we also do note that the redox-sensitive elements arsenic (As), iron (Fe), manganese (Mn), selenium (Se) and uranium (U) are significantly higher in the native groundwaters (NGWs) studied than in the Lumberyard Effluent used as a proxy for a possible treated effluent for this Scheme. This implies that the Injectate/NGW mixture will possibly exhibit an increase in the concentrations of these elements during storage.

In the absence of a trial with a real effluent which, in particular, has a redox potential and degree of chlorination (if any) which can be assumed to be truly representative of that applying in the real project we are not in a position to assess the degree of pickup into solution any re-extracted water of soluble As, Fe, Mn, Se or U more precisely.

That degree of pickup into solution would be the outcome of a geochemical balance between the amounts leached out of the aquifer lithology and the degree of precipitation of Fe and the degree of adsorption of As, Mn, Se and U both onto the native solids of the aquifer – particularly the pre-existing hydrous oxides of Fe and onto the hydrous oxides Fe and Al oxides predicted to be precipitated by our PHREEQC modeling of the injection scenario. As the elements As, Se and U would be largely present as negatively charged anionic species and the Fe and Al hydrous oxides would most likely be largely positively charged at the observed pHs, the degree of removal from solution by adsorption may be very significant.

It is assumed likely that real Injectate will have a much higher Eh than the Lumber Yard effluent and this suggests levels of dissolved Fe and Mn will be reduced in the stored Injectate over the original native levels (due to oxidation and precipitation).

The potential for DBPs formation/ingrowth in the aquifer is a key concern for the regulators.

Unfortunately we did not see any evidence to conclude that the single Lumber Yard effluent sample is a satisfactory proxy for DBP production given that PWR reported a Cl_2 residual of only 0.02 mg/L and WSE a confirming value of 0.015 mg/L – rather than the 1.0 mg/L or higher considered likely to apply to an actual Injectate. Furthermore, strangely the Lumber Yard Effluent did not contain detectable Haloacetic Acids (HAAs) nor Trihalomethanes (at least at the laboratory Method Resolution Limits; MRLs).

This greatly limits the precision of any statements we can make about the potential for the ingrowth of chlorination-induced DBPs during aquifer storage.

Certainly the high DOC of the Lumber Yard effluent (6.1 mg/L) and the even higher number suggested for the real Effluent by the June 2012 RMC Water and Environment technical memorandum (i.e. 9.5 mg/L) suggests that DBP production could be potentially be higher than was observed for the single grab sample of Lumber Yard effluent.

We also note that if chlorination was employed to disinfect the Injectate, as seems likely, thereby leading to DBP ingrowth (and decay) within the aquifer; this could potentially mandate re-use by drip, rather than spray irrigation due to the potential risk to the public from inhalation of spray drift containing DBPs.

Drip irrigation systems are more expensive to maintain than spray irrigation systems, particularly in respect of biofouling control and corrosion (due to their proximity to the soil), and are less mobile than spray irrigation systems. This is a factor which should be carefully considered if re-extraction is considered a likely option and wherever chlorination of the Injectate is unavoidable for any reason.

To further investigate the issue of DBPs in re-extracted water intended for some reuse e.g. drip irrigation of municipal parks and gardens it would be necessary to:

1. determine whether chlorination was to be mandatory for the Injectate prior to the injection and if it were; then
2. conduct a separate study to determine the typical degrees of DBP ingrowth and decay during aquifer storage,

in order to identify whether the storage timescale in a particular area of the aquifer could be extended to allow decay of DBPs to acceptable levels (in the specified reuse context).

Some References

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Sincerely

Dr. Stephen A. Short

Director