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Metropolitan Water Reclamation District of Greater Chicago

RESEARCH AND DEVELOPMENT DEPARTMENT

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REPORT ON ELEVATED LEVELS OF COPPER IN HANOVER PARK WATER RECLAMATION PLANT EFFLUENT FROM DECEMBER 1998 THROUGH JULY 1999

November 2000

Metropolitan Water Reclamation District of Greater Chicago
100 East Erie Street Chicago, IL 60611-2803 (312) 751-5600

REPORT ON ELEVATED LEVELS OF COPPER IN HANOVER PARK WATER RECLAMATION PLANT EFFLUENT FROM DECEMBER 1998 THROUGH JULY 1999

By

David T. Lordi
Research Scientist III

Bernard Sawyer
Coordinator of Research

Prakasam Tata
Assistant Director of Research and Development
Environmental Monitoring and Research Division

Research and Development Department
Richard Lanyon, Director

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DISCLAIMER

SUMMARY AND CONCLUSIONS

During the month of May 1999, the Maintenance and Operations (M&O) Department personnel at the Hanover Park Water Reclamation Plant (WRP) noticed that the final effluent copper concentrations had a number of daily values which were greater than 0.020 mg/L, and there was concern that the monthly average National Pollutant Discharge Elimination System (NPDES) permit limit for copper, of 0.027 mg/L, would be exceeded. Due to the need to maintain compliance with the effluent copper limit and the close tolerance between the concentration limit and the actual concentrations, variability in the effluent copper concentration is also of concern. For these reasons, the Research and Development (R&D) Department investigated the elevated copper concentrations. In order to determine the possible cause of the variations, the following investigations were initiated:

1. A review of operational practices and historical data for the Hanover Park WRP.
2. A study of the copper removal through the tertiary filters at the Hanover Park WRP.
3. Potable water in the area was sampled and analyzed for copper concentration.

4. The Industrial Waste Division (IWD) reviewed past records for and sampled possible industrial sources of copper.

5. The Analytical Laboratories Division (ALD) reviewed the analytical methodology in use at the John E. Egan Laboratory.

A review of the historical data of copper in the raw sewage and final effluent of the Hanover Park WRP showed that the influent copper concentration was higher in 1999 than in 1998, but was comparable to concentrations observed in 1996 and 1997. However, no elevated levels of final effluent copper were observed in 1996 and 1997. Effluent copper levels increased in December 1998 and continued at an increased level through June 1999. During the first six months of 1999, all the final effluent copper monthly averages were 0.02 mg/L or greater. However, the effluent copper values suddenly decreased on July 8, 1999 and continued to stay generally below 0.02 mg/L for the remainder of 1999. Despite this decrease, the average influent copper concentrations since July 8, 1999, were comparable to those, or slightly higher than those occurring in the first half of 1999.

Based on a review of the operational practices followed by the Hanover Park WRP staff, such as bypassing a portion of the secondary effluent around the tertiary filters, and discharge of the retention pond effluent directly into the final outfall, operational practices did not appear to cause the elevated levels of effluent copper in the first half of 1999.

Examination of potable water supply systems in the Hanover Park WRP service area and total copper concentrations in the potable water revealed that no changes were made in either the treatment or distribution practices in the service area. The total copper concentration in the potable water samples varied considerably. However, as no significant changes were made in the treatment and distribution practices of potable water, potable water used in the Hanover Park WRP service area was not found to be a cause for the elevated levels of effluent copper during the first half of 1999.

Sampling conducted by the IWD at three known industrial users located in the Hanover Park WRP service area revealed that the elevated effluent copper levels observed in May 1999 were not due to increased copper in their discharges.

A study of the removals of copper through the tertiary filter was conducted over the period of June 25, 1999 through July 23, 1999. One pair of filters had been recently reconstructed with new media, and this compared to a pair of original filters with old media. There was no difference in the copper or suspended solids of the effluents between the reconstructed and original filters. The soluble copper fraction was 30 to 41 percent of the total copper, with an average soluble concentration of approximately 0.008 mg/L in both the filter influents (secondary effluent) and filter effluents.

A sudden decrease in copper concentrations in the secondary effluent, filter effluent, and final effluent occurred on July 8 and 9, 1999. In general, the daily values decreased from greater than 0.025 mg/L to less than 0.020 mg/L. This decreased level has continued through 1999.

The increase in the final effluent copper concentrations observed beginning in December 1998, and its sudden decrease beginning July 8-9, 1999, in the absence of any operational changes at the WRP, suggested a possible analytical connection. The John E. Egan Laboratory also provides the analytical support to the other three North Area WRPs (John E. Egan, James C. Kirie, and North Side). A review of the July 1999 effluent copper data for the three other North Area WRPs showed that all three WRPs followed the same dramatic decrease in effluent copper of approximately 80 percent over the same period of a couple of days as the Hanover Park WRP experienced. Since such an occurrence happening simultaneously is highly improbable, it is speculated that the increase observed in December 1998 through June 1999 and the decrease in July 1999 may be the result of a laboratory abnormality or artifact.

A review of quality control procedures, calibration standards, and instrumentation, while uncovering some shortcomings in the procedures, did not provide any conclusive evidence as to whether laboratory abnormalities were the cause for either the initial increase or the sudden decrease in the Hanover Park WRP effluent copper.

Based upon the recommendation of the Quality Assurance Coordinator, the John E. Egan Laboratory has implemented additional quality control measures including analysis of a method blank with each sample batch, and use of a low-level copper check standard.

In conclusion, no definitive explanation has been found to explain the increase in final effluent copper which occurred at the Hanover Park WRP between December 1998 and July 1999. However, evidence suggests that it may have been due to a laboratory abnormality related to analyzing for copper concentrations that are very close to the analytical detection limit of the method.

INTRODUCTION

The Hanover Park WRP has, as a part of its NPDES permit, effluent limits for copper of 0.044 mg/L daily maximum and 0.027 mg/L as a monthly average. During the month of May 1999, the M&O Department personnel at the Hanover Park WRP noticed that a number of daily values were occurring in the range of 0.020 and 0.036 mg/L. The concern was the possible exceedence of the monthly average limit. This set into motion a number of actions to determine the possible cause of the elevated effluent copper concentrations. This included a review of the historical data, WRP operating procedures, and an investigation of possible industrial and potable water sources of copper. In addition, several specific studies were carried out, including an evaluation of the analytical methodology and a closer look at the copper removal by the tertiary filters.

This report presents the findings from these various studies and investigations.

RESULTS

Hanover Park WRP Monitoring - Historical Data

As part of the investigation of possible causes of the elevated copper final effluent concentrations observed in early 1999, especially May 1999, a review of the historical data for the Hanover Park WRP raw sewage and final effluent was undertaken.

HANOVER PARK WRP RAW SEWAGE COPPER

A review of the raw sewage copper values since 1992 was made in order to determine if there has been an increase in the influent copper levels which may be contributing to the increase in effluent copper levels. The monthly average influent copper values are presented in Table 1 for the period of 1992 through 1999. The copper levels seemed to be higher during 1996 to 1999 as compared to 1993 through 1995. The annual copper averages ranged from 0.079 to 0.100 mg/L for 1996-1999 vs. 0.070 to 0.073 mg/L for 1993-1995. Although the monthly average copper levels were higher in the latter part of 1998 and first part of 1999 as compared to the first half of 1998, these levels were similar to those observed in 1996 and 1997.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 1

HANOVER PARK WRP RAW SEWAGE MONTHLY MEAN COPPER CONCENTRATION*

	1992	1993	1994	1995	1996	1997	1998	1999
January	0.114	0.045	0.049	0.083	0.078	0.065	0.053	0.088
February	0.099	0.076	0.066	0.062	0.079	0.063	0.061	0.073
March	0.080	0.054	0.059	0.068	0.086	0.081	0.058	0.080
April	0.083	0.066	0.057	0.067	0.072	0.101	0.050	0.070
May	0.089	0.095	0.061	0.077	0.086	0.115	0.101	0.086
June	0.086	0.095	0.082	0.100	0.049	0.121	0.077	0.110
July	0.076	0.090	0.097	0.086	0.068	0.156	0.082	0.099
August	0.068	0.064	0.067	0.066	0.098	0.096	0.095	0.102
September	0.083	0.054	0.091	0.066	0.113	0.100	0.091	0.102
October	0.074	0.064	0.091	0.069	0.113	0.099	0.097	0.116
November	0.044	0.055	0.068	0.060	0.112	0.097	0.092	0.094
December	0.057	0.101	0.054	0.074	0.091	0.110	0.094	0.094
Mean	0.079	0.072	0.070	0.073	0.087	0.100	0.079	0.093
Min.	0.044	0.045	0.049	0.060	0.049	0.063	0.050	0.070
Max.	0.114	0.101	0.097	0.100	0.113	0.156	0.101	0.116

*Concentration in mg/L.

The influent copper concentrations that occurred in the first part of 1999 do not account for the increased final effluent values in 1999, since during the 1996-1998 period the effluent copper was low, generally less than 0.02 mg/L, even though the influent copper was similar to 1999.

HANOVER PARK WRP RAW SEWAGE SUSPENDED SOLIDS

The monthly average suspended solids values from 1992 through 1999 are summarized in Table 2. A noticeable increasing trend of raw sewage suspended solids from 1992 through 1997 was observed. The monthly averages then exhibited a decreasing trend in 1998 and 1999. The raw sewage suspended solids in the period of 1998 to June 1999 had an annual average of approximately 160 mg/L, as compared to 222 mg/L observed in 1996 through 1997. The trend in the last four years is similar to that observed for the raw sewage copper. The two years of highest suspended solids (1996, 1997) were also the two years for highest copper in the raw sewage.

HANOVER PARK WRP RAW SEWAGE METALS

In order to evaluate whether there was any unusual pattern in the raw sewage that could be attributed to industrial or other activity, the data for other metals collected for the raw sewage was reviewed for the period of June 1998 through

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TABLE 2

HANOVER PARK WRP RAW SEWAGE MONTHLY MEAN SUSPENDED SOLIDS CONCENTRATION*

	1992	1993	1994	1995	1996	1997	1998	1999
January	168	91	158	209	159	150	136	196
February	159	225	136	131	146	152	125	156
March	115	96	205	137	159	152	122	143
April	108	112	121	145	194	322	108	127
May	104	149	93	181	212	257	240	151
June	104	236	140	200	153	333	186	172
July	100	166	215	218	163	356	178	210
August	62	159	98	172	295	192	185	209
September	107	116	189	112	259	178	161	174
October	87	102	159	138	272	182	163	223
November	96	72	134	118	260	220	171	174
December	97	269	141	99	270	299	172	298
Mean	109	149	149	155	212	233	162	186
Min.	62	72	93	99	146	150	108	127
Max.	168	269	215	218	295	356	240	298

*Concentration in mg/L.

July 1999. Samples are analyzed for other metals, in addition to copper, once a week. The monthly average concentrations of copper, iron, manganese, nickel, zinc, and hexavalent chromium in these samples are presented in Table 3. Other metals, such as cadmium and lead, were generally at nondetectable levels. The high average values observed for the month of June 1999 are due to one sample, collected June 1, 1999, which had unusually high values of many of the metals. Excluding this sample, the monthly average concentrations for June 1999 would be similar to the other months. A review of the data in Table 3 does not indicate any systematic change in raw sewage metals that would indicate any unusually high industrial waste discharges of metals during the December 1998 through May 1999 period.

HANOVER PARK WRP EFFLUENT COPPER

The Hanover Park effluent total copper values were also reviewed for 1992 through 1999, and the monthly average values are presented in Table 4. As can be seen, the monthly average effluent copper has generally been below 0.020 mg/L through the end of 1998. These data indicate that an increasing trend in effluent copper levels started in December 1998 and continued into 1999. Prior to December 1998, the majority of the

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TABLE 3

HANOVER PARK WRP RAW SEWAGE MONTHLY MEAN METALS CONCENTRATION*

Month	Cu mg/L	Fe mg/L	Mn mg/L	Ni mg/L	Zn mg/L	Cr^{6+} µg/L
June 1998	0.097	0.99	0.067	0.00	0.116	3.5
July 1998	0.085	1.29	0.055	0.00	0.115	0.5
Aug. 1998	0.125	1.41	0.061	0.01	0.146	0.0
Sept. 1998	0.088	0.94	0.054	0.00	0.110	1.1
Oct. 1998	0.083	0.79	0.058	0.00	0.099	0.0
Nov. 1998	0.109	1.08	0.081	0.01	0.108	1.0
Dec. 1998	0.083	0.93	0.061	0.00	0.101	1.0
Jan. 1999	0.087	0.75	0.064	0.01	0.097	0.0
Feb. 1999	0.067	0.72	0.063	0.00	0.077	0.8
March 1999	0.080	0.75	0.060	0.00	0.088	1.0
April 1999	0.072	0.89	0.056	0.00	0.076	0.9
May 1999	0.093	1.03	0.074	0.00	0.082	0.0
June 1999	0.226	4.81	0.111	0.01	0.244	1.1
(June 1999)**	(0.095)	(1.43)	(0.077)	(0.01)	(0.099)	(0.0)
July 1999	0.088	1.03	0.046	0.01	0.134	0.0

*Average of 3 to 5 values per month.
**(With June 1st sample excluded.)

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TABLE 4

HANOVER PARK WRP EFFLUENT MONTHLY MEAN COPPER CONCENTRATION*

	1992	1993	1994	1995	1996	1997	1998	1999
January	0.010	0.007	0.004	0.012	0.019	0.015	0.018	0.023
February	0.015	0.009	0.010	0.014	0.024	0.014	0.019	0.020
March	0.018	0.015	0.007	0.017	0.019	0.017	0.023	0.025
April	0.016	0.009	0.006	0.017	0.017	0.015	0.017	0.020
May	0.013	0.014	0.008	0.017	0.019	0.018	0.017	0.027
June	0.013	0.009	0.006	0.019	0.005	0.015	0.013	0.027
July	0.012	0.008	0.009	0.009	0.004	0.013	0.006	0.019
August	0.013	0.004	0.015	0.006	0.006	0.014	0.015	0.011
September	0.013	0.007	0.009	0.003	0.006	0.011	0.013	0.011
October	0.008	0.010	0.011	0.009	0.012	0.014	0.016	0.011
November	0.005	0.005	0.004	0.012	0.019	0.013	0.015	0.008
December	0.008	0.006	0.007	0.018	0.012	0.013	0.022	0.012
Mean	0.012	0.009	0.008	0.013	0.014	0.014	0.016	0.018
Min.	0.005	0.004	0.004	0.003	0.004	0.011	0.006	0.008
Max.	0.018	0.015	0.015	0.019	0.024	0.018	0.023	0.027

*Concentration in mg/L.

monthly average copper values were less than 0.02 mg/L. During the first half of 1999, all of the monthly average values were 0.02 mg/L or greater.

This increase in final effluent copper concentrations is even more evident when daily values are examined. Table 5 presents daily values of Hanover Park WRP final effluent copper from October 1998 through June 1999. It can be seen from this data that the final effluent copper concentrations reached very high levels in the range of 0.022 to 0.038 mg/L during June 1999. As can also be seen, the number of daily values exceeding 0.020 mg/L increased beginning in December 1998, as compared to the October and November 1998 values. Then, in June 1999 all of the effluent daily copper values were greater than 0.020 mg/L. There were also several values greater than 0.030 mg/L in May and June 1999.

HANOVER PARK WRP EFFLUENT SUSPENDED SOLIDS

Table 6 shows the monthly average effluent suspended solids concentrations for 1992 through 1999. Higher suspended solids generally occurred during the high flow months of January through May.

The effluent suspended solids were slightly lower for the first six months of 1999 (average 6.0 mg/L) as compared to the

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TABLE 5

DAILY FINAL EFFLUENT COPPER CONCENTRATIONS AT THE HANOVER PARK WRP

Day	Copper mg/L								
	Oct. 1998	Nov. 1998	Dec. 1998	Jan. 1999	Feb. 1999	Mar. 1999	Apr. 1999	May 1999	June 1999
1	0.013	0.022	0.009	---	0.010	0.021	0.028	---	0.025
2	---	0.023	0.016	---	0.013	0.022	---	0.018	0.023
3	---	0.028	0.016	0.022	0.015	0.021	---	0.017	0.028
4	0.012	0.012	---	0.024	0.009	0.020	0.028	---	---
5	0.016	0.015	---	0.024	---	---	0.012	0.036	---
6	0.012	---	0.016	0.029	---	---	0.013	0.032	0.029
7	0.011	---	0.026	0.026	0.013	0.022	0.014	0.029	0.024
8	0.011	0.012	0.020	---	0.015	0.033	0.015	---	0.026
9	---	0.023	0.021	---	0.011	0.028	---	0.025	0.027
10	---	0.019	0.024	0.025	0.025	0.020	---	0.028	0.026
11	0.013	0.013	---	0.023	0.030	0.021	0.012	0.029	---
12	0.014	0.017	---	0.023	---	---	0.019	0.028	---
13	0.012	---	0.021	0.026	---	---	0.031	0.022	0.025
14	0.017	---	0.031	0.024	0.023	0.023	0.026	---	0.024
15	0.015	0.014	0.027	---	0.023	0.025	0.026	---	0.034
16	---	0.015	0.025	---	0.021	0.025	---	0.031	0.025
17	---	0.014	0.024	0.022	0.023	0.019	---	0.032	0.022
18	0.017	0.014	---	0.024	0.021	0.033	0.028	0.028	---
19	0.017	0.014	---	0.025	---	---	0.025	0.028	---
20	---	---	0.023	0.020	---	---	0.029	0.030	0.038

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TABLE 5 (Continued)

DAILY FINAL EFFLUENT COPPER CONCENTRATIONS AT THE HANOVER PARK WRP

	Copper mg/L								
Day	Oct. 1998	Nov. 1998	Dec. 1998	Jan. 1999	Feb. 1999	Mar. 1999	Apr. 1999	May 1999	June 1999
21	0.019	---	0.025	0.019	0.031	0.024	0.026	---	0.025
22	0.016	0.011	0.027	---	0.029	0.028	0.014	---	0.028
23	0.016	0.008	0.030	---	0.019	0.028	---	0.022	0.023
24	---	0.010	0.022	0.019	0.023	0.029	---	0.024	0.030
25	0.016	0.007	---	0.017	0.024	0.022	0.016	0.025	---
26	0.025	0.008	---	0.024	---	---	0.018	0.029	---
27	0.023	---	0.028	0.024	---	---	0.016	0.022	0.026
28	0.026	---	0.022	0.019	0.023	0.027	0.013	---	0.029
29	0.025	0.010	0.018	---	---	0.028	0.013	---	0.028
30	---	0.013	0.017	---	---	0.028	---	0.029	0.030
31	---	---	0.023	0.025	---	0.030	---	0.022	---
Mean	0.016	0.015	0.022	0.023	0.020	0.025	0.020	0.027	0.027
Min.	0.011	0.007	0.009	0.017	0.009	0.019	0.012	0.017	0.022
Max.	0.026	0.028	0.031	0.029	0.031	0.033	0.031	0.036	0.038

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TABLE 6

HANOVER PARK WRP EFFLUENT MONTHLY MEAN SUSPENDED SOLIDS CONCENTRATION*

	1992	1993	1994	1995	1996	1997	1998	1999
January	2	2	7	4	5	11	10	7
February	3	2	7	8	5	12	11	6
March	3	6	4	6	8	8	11	6
April	2	4	9	7	11	8	9	7
May	2	5	1	4	10	5	5	5
June	3	6	3	4	7	1	4	5
July	2	2	1	3	4	1	3	2
August	2	2	3	4	2	1	2	2
September	2	2	3	1	2	1	2	2
October	3	2	4	4	2	1	7	2
November	3	2	6	3	3	2	7	2
December	3	4	7	3	6	8	4	6
Mean	3	3	5	4	5	5	6	6
Min.	2	2	1	1	2	1	2	2
Max.	3	6	9	8	11	12	11	7

*Concentration in mg/L.

first six months of 1998 (8.3 mg/L). In contrast, the effluent copper values did not decrease in 1999, but instead showed an increase.

The daily effluent suspended solids values for the period of October 1998 through June 1999 are presented in Table 7. The daily suspended solids values do not show the same type of increasing trend that was noted for the effluent copper values. The daily suspended solids values range between 2 and 15 mg/L during October and November 1998 and between 0 and 12 mg/L during May and June 1999. Thus, the increase in the effluent copper concentrations could not be attributed to the effluent suspended solids.

Potable Water Supplies

In order to investigate the possibility that copper levels in the potable water supply were causing an increase in copper loadings to the WRP, grab samples of potable water were taken at different locations within the Hanover Park WRP service area. The service area includes four different municipalities: Hanover Park, parts of Bartlett, Streamwood, and Schaumburg. Hanover Park, Streamwood, and Schaumburg obtain their drinking water from the City of Chicago through the North Suburban Municipal Joint Action Water Agency. The City

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TABLE 7

DAILY FINAL EFFLUENT SUSPENDED SOLIDS CONCENTRATIONS AT THE HANOVER PARK WRP

	Suspended Solids (mg/L)								
Day	Oct. 1998	Nov. 1998	Dec. 1998	Jan. 1999	Feb. 1999	Mar. 1999	Apr. 1999	May 1999	Jun. 1999
1	2	11	3	---	7	4	9	---	4
2	---	9	3	---	10	4	---	3	7
3	---	7	2	14	18	5	---	4	4
4	3	8	---	11	6	4	9	---	---
5	5	6	---	11	---	---	6	5	---
6	3	---	4	9	---	---	2	5	8
7	2	---	11	8	7	6	4	2	4
8	3	7	3	---	3	8	5	---	5
9	---	8	4	---	3	10	---	0	2
10	---	10	4	11	3	6	---	0	3
11	4	7	---	11	7	4	9	2	---
12	5	7	---	5	---	---	4	7	---
13	4	---	3	4	---	---	4	4	3
14	3	---	3	4	11	8	4	---	6
15	5	10	3	---	6	10	8	---	6
16	---	9	3	---	4	9	---	8	9
17	---	8	2	5	5	6	---	9	8
18	8	6	---	7	3	3	9	7	---
19	14	7	---	5	---	---	7	9	---
20	---	---	4	5	---	---	11	6	12
21	15	---	4	6	5	8	12	---	6
22	14	---	4	---	6	6	9	---	3
23	14	2	4	---	6	4	---	7	4
24	---	3	5	9	6	9	---	4	0
25	11	2	---	6	5	5	14	3	---
26	7	3	---	5	---	---	8	2	---
27	4	---	4	5	---	---	8	2	0
28	5	---	6	5	7	0	3	---	3
29	8	3	4	---	---	3	5	---	3

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 7 (Continued)

DAILY FINAL EFFLUENT SUSPENDED SOLIDS CONCENTRATIONS AT THE HANOVER PARK WRP

Day	Suspended Solids (mg/L)								
	Oct. 1998	Nov. 1998	Dec. 1998	Jan. 1999	Feb. 1999	Mar. 1999	Apr. 1999	May 1999	Jun. 1999
30	---	4	4	---	---	3	---	2	3
31	---	---	8	9	---	3	---	4	---
Mean	7	7	4	7	6	6	7	4	5
Min.	2	2	2	4	3	0	2	0	0
Max.	15	11	11	14	18	10	14	9	12

of Chicago has been adding a polyphosphate to the finished water for corrosion control since 1994. The Village of Bartlett obtains water from the City of Elgin and from its own well water system. The City of Elgin does not treat the water with a polyphosphate corrosion control agent.

Grab samples of tap water were taken from the faucets of commercial establishments in each of the above four municipal areas. In general, with the exception of the sample taken on August 27, 1999 from BART_TAP(A), all the water samples were taken without first flushing the line. The results of the copper analysis of these samples are presented in Table 8.

The results are generally greater than 0.02 mg Cu/L. It is not known how long the water was stagnating in the pipes before the samples were taken. As may be seen for the BART_TAP(A) location, extremely high copper concentrations were observed initially (2.16 and 1.034 mg/L). The sample taken after the line was allowed to purge thoroughly (August 27, 1999) had a copper concentration of 0.001 mg/L.

Based upon verbal contacts with the various suburbs, it does not appear that any changes in drinking water sources or treatments occurred in the past few years. Since drinking water normally does not stagnate for any length of time in the distribution system because it is constantly being drawn by

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TABLE 8

COPPER CONCENTRATION[1] IN TAP WATER SAMPLES FROM COMMERCIAL ESTABLISHMENTS IN THE HANOVER PARK WRP SERVICE AREA

Sample Location[2]	6/30/99	7/14/99	8/3/99	8/27/99
HP_TAP	0.1760	0.089	NS[3]	NS
BART_TAP(A)	2.16	NS	1.034	0.001
BART_TAP(B)	NS	1.141	NS	NS
BART_TAP(C)	NS	NS	NS	0.001
BART_TAP(D)	NS	NS	NS	0.001
STRE_TAP	0.0032	0.021	NS	NS
SCHA_TAP	0.059	0.025	NS	NS

[1]Concentrations in mg/L.
[2]HP_TAP: Menard's in Hanover Park.
BART_TAP(A): White Hen in Bartlett.
BART_TAP(B): Ace Hardware in Bartlett.
BART_TAP(C): Village of Bartlett water treatment plant wet well.
BART_TAP(D): Village of Bartlett water tower.
STRE_TAP: Wal-Mart in Streamwood.
SCHA_TAP: Schaumburg Fire Department Station House.
[3]NS = No sample.

the community and it has a very low background concentration (0.011 mg/L), it does not appear to be the cause of the elevated copper concentrations in the Hanover Park WRP effluent.

Industrial Contribution of Copper

In response to the elevated effluent copper levels observed during May 1999, the IWD carried out an investigation of known industrial copper sources. Table 9 identifies four known companies and provides annual discharge loadings from each over the period of 1998 through May 1999. The 1999 loadings are estimated based on 1999 average effluent copper concentrations in the samples analyzed and 1998 flows. The number of companies has decreased from four in 1998 to three in 1999. The total pounds of copper per year discharged by known industries in the Hanover Park WRP service area also decreased in 1999 as compared to 1998.

In addition, a door-to-door inspection was carried out of all tenants located in the Centex Industrial Park, which is in the Hanover Park WRP service area. No new industrial sources were found. The three existing sources are Electro Circuits, Senior Flexonics, and Eagle Electronics. Dedicated automatic samplers were installed in Electro Circuits (since December

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TABLE 9

HANOVER PARK WATER RECLAMATION PLANT INDUSTRIAL USERS SAMPLED BY THE DISTRICT
1998 THROUGH 1999

Year	Industrial User	Outlet(s)	Analyses	Flow (GPY)	Average Cu Concentration (mg/L)	Cu (lbs/yr)
1998	Eagle Electronics	1A	9	17,941,000	0.20	30
1998	Electro-Circuits Inc.	1A	7	8,076,000	1.30	88
1998	Komet of America Inc.	1A	4	2,218,000	0.05	1
1998	Senior Flexonics Inc.	1A, 3A	9	61,837,764	0.09	49
	4 Companies		29	90,072,764	0.22	168
1999 (est.)	Eagle Electronics	1A	4	17,941,000*	0.23	35
1999 (est.)	Electro-Circuits Inc.	1A	121	8,076,000*	1.02	69
1999 (est.)	Senior Flexonics Inc.	1A, 3A	8	61,837,764*	0.06	33
	3 Companies		133	87,854,764	0.19	137

*1998 flows used for calculating copper loading.

21, 1998) and in a sewer downstream of the discharges from Senior Flexonics and Eagle Electronics (since May 24, 1999).

The IWD also maintains automatic samplers in the two main interceptors serving the Hanover Park WRP. In the past, these have been used to assist in detecting industrial discharges. A review of the data from these two sampling stations for the period of October 1998 through July 1999 did not reveal any increases in copper concentrations that would explain the increased effluent copper concentrations at the Hanover Park WRP.

In 1999 and 1998, the estimated and actual industrial loading of copper was 137 and 168 lbs/year, respectively, compared to the total copper loading to the WRP of 2758 and 2434 lbs/year, respectively. Thus, known industrial discharges of copper do not appear to be the problem, as they only account for 5 to 7 percent of the copper entering the Hanover Park WRP.

Operational Practices at the Hanover Park WRP

In an attempt to determine if any operational changes at the Hanover Park WRP could have affected final effluent copper concentrations, a review of the operational practices at the WRP was made with Mr. Brett Garelli, Plant Manager. Two practices which had the potential to contribute to higher copper levels in the final effluent were discussed.

The first operational practice is the periodic discharge of effluent from the retention pond directly into the final outfall, where it is mixed with the tertiary effluent.

The second operational practice was the necessity of having a portion of the secondary effluent bypass the tertiary filters. This is due to the inadequate capacity of the filters to accept all of the secondary effluent flow. It should be noted that additional filters were under construction during the period elevated copper levels were noted.

RETENTION POND EFFLUENT

The quantity of retention pond effluent discharged directly to the outfall was similar during the first six months of 1999 (0 to 2.22 MGD) as compared to the first six months of 1998 (0 to 1.76 MGD) (Table 10). In fact, during May and June 1999, when the effluent copper levels were the highest, the operations staff ceased (after May 1, 1999) discharging retention pond effluent directly to the outfall.

During these months, retention pond effluent was periodically discharged to the head of the Hanover Park WRP into the wet well. M&O was requested to take grab samples of the pond

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 10

HANOVER PARK WRP RETENTION POND EFFLUENT DISCHARGED DURING 1998 AND 1999

Month	Average Retention Pond Flow To Head Of Plant (MGD)	Average Retention Pond Flow To Outfall (MGD)	Total WRP Discharge To Stream (MGD)
	1998		
Jan.	0.10 (11)[1]	1.76 (27)	12.71
Feb.	0.29 (8)	1.66 (26)	12.82
Mar.	0.00 (0)	1.56 (26)	12.90
Apr.	0.00 (0)	1.35 (29)	13.89
May.	0.63 (10)	0.46 (13)	11.03
Jun.	<0.01 (3)	0.00 (0)	8.64
Jul.	0.04 (3)	0.00 (0)	8.15
Aug.	0.00 (0)	0.00 (0)	7.52
Sep.	0.00 (0)	0.00 (0)	7.24
Oct.	0.91 (10)	0.44 (7)	9.93
Nov.	0.42 (11)	0.00 (0)	8.53
Dec.	0.10 (2)	0.00 (0)	8.06
	1999		
Jan.	0.03 (1)	1.85 (10)	12.10
Feb.	0.20 (5)	0.29 (4)	11.10
Mar.	0.0 (0)	0.38 (12)	10.90
Apr.	0.71 (10)	2.22 (22)	14.57
May	0.55 (13)	0.05 (1)	10.27
Jun.	1.46 (18)	0.0 (0)	10.77
July	0.0 (0)	0.0 (0)	6.93
Aug.	0.0 (0)	0.0 (0)	6.73
Sep.	0.0 (0)	0.0 (0)	6.97
Oct.	0.24 (11)	0.0 (0)	7.18

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 10 (Continued)

HANOVER PARK WRP RETENTION POND EFFLUENT DISCHARGED DURING 1998 AND 1999

Month	Average Retention Pond Flow To Head Of Plant (MGD)	Average Retention Pond Flow To Outfall (MGD)	Total WRP Discharge To Stream (MGD)
Nov.	0.0 (0)	0.0 (0)	6.05
Dec.	0.35 (21)	0.0 (0)	7.52

[1]Values in parenthesis under this column are number of days during the month that had retention pond discharge to outfall.

effluent whenever it was returned to the WRP. These samples were analyzed for total copper. The results are presented in Table 11 for the period of June 5 through June 21, 1999. The values were between 0.019 and 0.031 mg/L, with an average of 0.026 mg/L, similar to the final effluent values and lower than the raw sewage copper concentration. Unfortunately, no copper data were available for 1998 to make a comparison.

From the data presented, which did not show any unusually high flows in 1999 as compared to 1998 nor higher concentrations of copper as compared to the final outfall, it is highly unlikely that the retention pond effluent being discharged to the head of the WRP or directly to the outfall was the cause of the elevated copper levels observed in May and June 1999.

SECONDARY EFFLUENT BYPASSING

The Hanover Park WRP flow data for 1998 and 1999 are presented in Tables 12 and 13, respectively. These tables include the monthly average flows of the secondary effluent filter bypass, the tertiary filter flow, the combined flow (tertiary filter flow plus secondary effluent filter by-pass), the retention pond flow to the outfall, and the total plant discharge.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 11

HANOVER PARK WRP RETENTION POND EFFLUENT TOTAL COPPER CONCENTRATION

Date	Total Copper (mg/L)
6/5/99	0.031
6/6/99	0.030
6/7/99	0.025
6/8/99	0.027
6/9/99	0.028
6/10/99	0.030
6/11/99	0.029
6/12/99	0.023
6/13/99	NS
6/14/99	0.024
6/15/99	0.025
6/16/99	NS
6/17/99	0.020
6/18/99	0.019
6/19/99	0.028
6/20/99	0.026
6/21/99	0.031
Minimum	0.019
Mean	0.026
Maximum	0.031

NS = No sample.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 12

HANOVER PARK WRP COPPER STUDY
FLOWS FOR VARIOUS STREAMS FOR 1998*

Month	Sec. Eff. Filter Bypass MGD	Tertiary Filter Flow MGD	Combined Flow** MGD	Retention Pond to Outfall MGD	Total Discharge MGD	Percent Bypass of Combined Flow	Percent Bypass of Total Flow	Percent Tertiary Filter Flow of Total Flow
January	1.10	9.85	10.95	1.76	12.71	10.05	8.65	77.50
February	1.76	9.40	11.16	1.66	12.82	15.77	13.73	73.32
March	1.67	9.67	11.34	1.56	12.90	14.73	12.95	74.96
April	2.18	10.36	12.54	1.35	13.89	17.38	15.69	74.59
May	1.10	9.47	10.57	0.46	11.03	10.41	9.97	85.86
June	0.19	8.45	8.64	0.00	8.64	2.20	2.20	97.69
July	0.08	8.07	8.15	0.00	8.15	0.98	0.98	99.02
August	0.08	7.44	7.52	0.00	7.52	1.06	1.06	98.94
September	0.06	7.18	7.24	0.00	7.24	0.83	0.83	99.03
October	0.93	8.56	9.49	0.44	9.93	9.80	9.37	86.20
November	0.97	7.56	8.53	0.00	8.53	11.37	11.37	88.63
December	0.08	7.98	8.06	0.00	8.06	0.99	0.99	98.88

*Data from M&O Department Monthly Plant Operating Data.
**Combined Flow = filter plus secondary effluent filter bypass flow.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 13

HANOVER PARK WRP COPPER STUDY
FLOWS FOR VARIOUS STREAMS FOR 1999*

Month	Sec. Eff. Filter Bypass MGD	Tertiary Filter Flow MGD	Combined Flow** MGD	Retention Pond to Outfall MGD	Total Discharge MGD	Percent Bypass of Combined Flow	Percent Bypass of Total Flow	Percent Tertiary Filter Flow of Total Flow
January	0.6	9.65	10.25	1.85	12.10	5.85	4.95	79.7
February	0.98	9.83	10.81	0.29	11.10	9.07	8.82	88.5
March	1.78	8.74	10.52	0.38	10.90	16.92	16.33	80.2
April	2.63	9.72	12.35	2.22	14.57	21.30	18.04	66.7
May	1.20	9.02	10.22	0.05	10.27	11.75	11.70	87.9
June	1.04	9.73	10.77	0.00	10.77	9.66	9.66	90.3
July	0.07	6.86	6.93	0	6.93	1.0	1.0	99.0
August	0.04	6.69	6.73	0	6.73	0.6	0.6	99.4
September	0	6.97	6.97	0	6.97	0	0	100.0
October	0	7.18	7.18	0	7.18	0	0	100.0

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 13 (Continued)

HANOVER PARK WRP COPPER STUDY
FLOWS FOR VARIOUS STREAMS FOR 1999*

Month	Sec. Eff. Filter Bypass MGD	Tertiary Filter Flow MGD	Combined Flow** MGD	Retention Pond to Outfall MGD	Total Discharge MGD	Percent Bypass of Combined Flow	Percent Bypass of Total Flow	Percent Tertiary Filter Flow of Total Flow
November	0	6.05	6.05	0	6.05	0	0	100.0
December	0.10	7.42	7.52	0	7.52	1.33	1.33	98.7

*Data from M&O Department Monthly Plant Operating Data.
**Combined Flow = filter plus secondary effluent filter bypass flow.

From these data, it is observed that the bypassing of the filters in 1999 was similar to the 1998 practice, when elevated copper levels were not observed. The percentage of bypass flow to the combined flow varied from 2.20 to 17.38 percent in the first six months of 1998 and from 5.85 to 21.30 percent in the first six months of 1999.

Tertiary Filter Sampling and Associated Influent and Effluent Copper Concentrations

As previously discussed, the final effluent copper levels seemed to start increasing in December 1998. It was learned from Mr. Brett Garelli, Plant Manager, at the Hanover Park WRP, that just prior to December 1998, two of the six rapid sand filters had been reconstructed, including replacement of the filter media, and placed back into service. Due to the possibility that the reconstructed filters may have contributed to the increased final effluent copper levels, a study was initiated to sample the influent and effluent from the reconstructed Filters Nos. 1 and 2 and the original Filters No. 3 and 4. The influent to Filters 1 and 2 is the secondary effluent from Batteries A/B, and the influent to Filters 3 and 4 is the secondary effluent from Batteries C/D. Automatic 24-hour composite samplers were installed on the two secondary effluent streams ahead of the filters. M&O personnel installed similar composite samplers in the effluent channels from Filters 1 and 3.

A study began on June 25, 1999 in which separate 24-hour composite samples of the filter influents and effluents from the reconstructed and original filters were collected. The sampling was continued through July 23, 1999. The collected samples were analyzed for total copper, soluble (nonfilterable) copper, and several other metals. In addition, suspended solids were determined on the filter effluent samples collected over the period July 10 through July 23, 1999.

Tables 14, 15, and 16 present the results of analysis for total copper, soluble copper, and suspended solids, respectively. These tables also include data for the final outfall.

The overall averages showed no difference in effluent total copper between the reconstructed and original filters with the effluent from Filters 1 and 2 averaging 0.022 mg/L and Filters 3 and 4 averaging 0.021 mg/L over the period of the study. The final outfall total copper averaged 0.021 mg/L for the same period.

Similarly, the influent to the filters were the same, with the total copper averaging 0.023 mg/L for both filter influents.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 14

TOTAL COPPER CONCENTRATIONS IN THE INFLUENT AND EFFLUENT OF HANOVER PARK WRP FILTERS

	Total Copper (mg/L)				
Date	Influent Filter-1, 2	Effluent Filter-1, 2	Influent Filter-3, 4	Effluent Filter-3, 4	Final Outfall
6/25/99	0.031	0.035	0.026	0.022	NS
6/26/99	0.028	0.031	0.026	0.024	NS
6/27/99	0.031	0.038	0.033	0.026	0.026
6/28/99	0.028	0.033	0.031	0.026	0.029
6/29/99	0.038	0.030	0.030	0.029	0.028
6/30/99	0.028	0.027	0.031	0.028	0.030
7/1/99	0.032	0.027	0.024	0.034	0.028
7/2/99	0.029	0.031	0.029	0.033	NS
7/3/99	0.026	0.032	0.030	0.029	NS
7/4/99	0.033	0.027	0.033	0.031	0.028
7/5/99	0.028	0.025	0.029	0.031	0.025
7/6/99	0.029	0.028	0.029	0.026	0.023
7/7/99	0.026	0.025	0.031	0.027	0.026
7/8/99	0.028	0.016	0.027	0.014	0.027
7/9/99	0.018	0.015	0.013	0.013	NS
7/10/99	0.015	0.014	0.013	0.011	NS
7/11/99	0.016	0.012	0.013	0.010	0.013
7/12/99	0.016	0.015	0.016	0.015	0.013
7/13/99	0.015	0.015	0.014	0.013	0.014
7/14/99	0.020	0.014	0.016	0.013	0.013
7/15/99	0.021	0.014	0.021	0.012	0.011
7/16/99	0.015	0.024	0.016	0.020	NS
7/17/99	0.018	0.029	0.015	0.018	NS
7/18/99	0.016	0.018	0.017	0.021	0.017
7/19/99	0.019	0.020	0.023	0.023	0.018
7/20/99	0.028	0.016	0.029	0.017	0.020
7/21/99	0.017	0.014	0.016	0.014	0.012
7/22/99	0.018	0.015	0.014	0.013	0.014
7/23/99	0.011	0.010	0.009	0.008	NS
Number	29	29	29	29	20
Mean	0.023	0.022	0.023	0.021	0.021
Min	0.011	0.010	0.009	0.008	0.011
Max	0.038	0.038	0.033	0.034	0.030
Mean 6/25-7/7/99	0.030	0.030	0.029	0.028	0.027
Mean 7/9-7/23/99	0.018	0.016	0.016	0.015	0.015

NS = No sample.

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 15

SOLUBLE COPPER CONCENTRATIONS IN THE INFLUENT AND EFFLUENT OF HANOVER PARK WRP FILTERS

	Soluble Copper (mg/L)				
Date	Influent Filter-1, 2	Effluent Filter-1, 2	Influent Filter-3, 4	Effluent Filter-3, 4	Final Outfall
6/25/99	0.009	0.016	0.006	0.006	NA
6/26/99	0.008	0.012	0.006	0.007	NA
6/27/99	0.008	0.009	0.007	0.007	NA
6/28/99	0.008	0.009	0.009	0.007	NA
6/29/99	0.010	0.010	0.007	0.007	NA
6/30/99	0.011	0.011	0.008	0.009	NA
7/1/99	0.011	0.010	0.009	0.009	0.009
7/2/99	0.011	0.011	0.009	0.010	NS
7/3/99	0.010	0.010	0.009	0.008	NS
7/4/99	0.010	0.009	0.007	0.008	0.007
7/5/99	0.009	0.010	0.006	0.006	0.007
7/6/99	0.009	0.009	0.006	0.007	0.006
7/7/99	0.009	0.009	0.007	0.007	0.007
7/8/99	0.009	0.010	0.007	0.009	NS
7/9/99	0.009	0.009	0.007	0.009	NS
7/10/99	0.008	0.009	0.007	0.006	NS
7/11/99	0.008	0.008	0.006	0.008	NS
7/12/99	0.008	0.008	0.007	0.007	NS
7/13/99	0.007	0.010	0.007	0.009	NS
7/14/99	0.008	0.008	0.007	0.013	NS
7/15/99	0.008	0.012	0.006	0.008	NS
7/16/99	0.006	0.006	0.005	0.006	NS
7/17/99	0.007	0.007	0.005	0.006	NS
7/18/99	0.006	0.006	0.005	0.014	NS
7/19/99	0.006	0.005	0.005	0.017	NS
7/20/99	0.006	0.006	0.006	0.007	NS
7/21/99	0.007	0.008	0.006	0.006	NS
7/22/99	0.006	0.006	0.005	0.007	NS
7/23/99	0.006	0.006	0.004	0.005	NS
Number	29	29	29	29	5
Average	0.008	0.009	0.007	0.008	0.007
Min	0.006	0.005	0.004	0.005	0.006
Max	0.011	0.016	0.009	0.017	0.009

NA = No analysis.
NS = No samples.

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TABLE 16

SUSPENDED SOLIDS CONCENTRATIONS IN THE INFLUENT AND EFFLUENT OF HANOVER PARK WRP FILTERS

	Total Suspended Solids (mg/L)				
Date	Influent Filter-1, 2	Effluent Filter-1, 2	Influent Filter-3, 4	Effluent Filter-3, 4	Final Outfall
7/1/99	10	NA	10	NA	3
7/2/99	8	NA	9	NA	NS
7/3/99	7	NA	16	NA	NS
7/4/99	7	NA	11	NA	2
7/5/99	8	NA	9	NA	3
7/6/99	6	NA	5	NA	2
7/7/99	6	NA	7	NA	2
7/8/99	9	NA	11	NA	3
7/9/77	8	NA	5	NA	NS
7/10/99	6	0	6	0	NS
7/11/99	7	0	4	0	2
7/12/99	6	2	7	2	1
7/13/99	6	3	7	2	3
7/14/99	6	AT_{20}	6	2	2
7/15/99	6	3	7	0	2
7/16/99	3	2	6	3	NS
7/17/99	6	2	6	3	NS
7/18/99	4	0	6	2	1
7/19/99	5	0	8	0	3
7/20/99	6	2	12	3	4
7/21/99	6	2	8	3	2
7/22/99	4	2	8	3	1
7/23/99	5	0	5	0	NS
Number	22	12	22	13	16
Average	6.4	1.5	7.9	1.8	2.3
Min	3	0	4	0	1
Max	10	3	16	3	4

NA = No analysis.
NS = No sample.
AT_{20} = Atypical value not included in average.

The suspended solids data show that the filters are removing particulate matter (Table 16). Over the period of July 10 through 23, 1999, the suspended solids in the influent to the filters averaged 5.4 and 6.9 mg/L for Filters 1 and 3, respectively. Suspended solids were removed by the filters, resulting in effluents averaging 1.4 and 1.6 mg/L for Filters 1 and 3, respectively. There was no significant difference in the percent suspended solids removed between the reconstructed (76 percent removal) and the original filters (78 percent removal).

The soluble copper, in which a sample is filtered through a 0.45 micron filter prior to analysis, averaged 0.008 and 0.007 mg/L for the influents and 0.009 and 0.008 mg/L for the filter effluents for Filters 1 and 3, respectively. The soluble copper concentrations are approximately 30 to 40 percent of the total copper concentration averages.

As will be noted from the total copper data in Table 14, a marked reduction in the copper levels occurred on July 8 and 9, 1999. This decrease occurred in all three process streams: the secondary effluents (influents to the filter), the filter effluents, and the final outfall. The daily total copper values dropped from a range of 0.022 to 0.038 mg/L (6/25/99-7/7/99) to a range of 0.008 to 0.029 mg/L (7/9/99-7/23/99) for the filter influents, filter effluents, and the final outfall samples. The total copper concentrations, except for an occasional value, remained at these low values for the remainder of the study period.

The average total copper concentrations over the period of June 25 through July 7, 1999 were between 0.027 and 0.030 mg/L for the filter effluents and final outfall (Table 14). These values are similar to the average monthly values (0.027 mg/L, Table 4) for the outfall observed for May and June 1999. In contrast, for the period July 9 through July 23, 1999, the average total copper concentrations for the filter effluents and final outfall ranged from 0.015 mg/L to 0.016 mg/L (Table 14). This is approximately a 44 to 41 percent decrease from the total copper levels observed in the previous months of May and June.

Analytical Methodology

As the elevated effluent copper levels that occurred during the period of December 1998 to July 8, 1999 could not be explained by either changes in plant operation protocols or industrial and drinking water sources, an examination of the analytical protocol followed by the John E. Egan WRP

Analytical Laboratory was made. The following is a description of this examination and observations made.

As previously discussed, a review of the Hanover Park WRP final outfall copper data showed that the final effluent copper started to increase around December 1998 in terms of the monthly average (Table 4). There was also an increase in the frequency of the number of daily values greater than 0.02 mg/L.

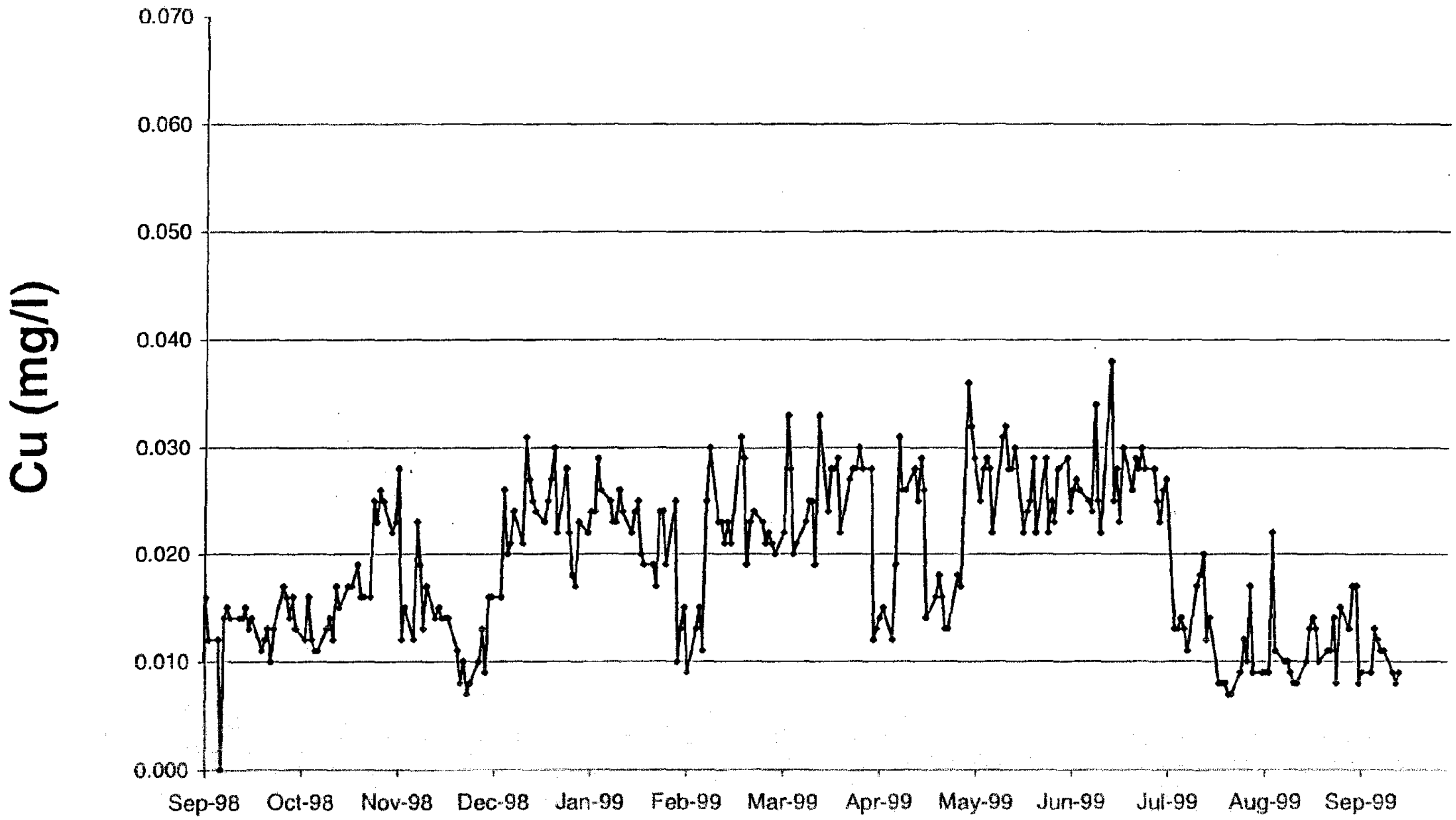
The daily effluent copper values for the Hanover Park WRP are plotted in Figure 1 for the period of September 1998 through September 1999. In addition, daily effluent copper values are plotted in Figures 2 and 3 for the John E. Egan and James C. Kirie WRPs for the same time period. The figures show that for all three WRPs there was an increase in effluent copper levels after December 1998, with a greater number of daily values exceeding 0.020 mg/L. The analysis of copper for all three of these WRPs is performed at the John E. Egan Laboratory.

In general, the daily variability of effluent copper values before and after December 1998 were similar, except there appears to be a shift upwards by approximately 0.010 mg/L between December 1998 and July 1999.

METROPOLITAN WATER RECLAMATION OF GREATER CHICAGO

FIGURE 1

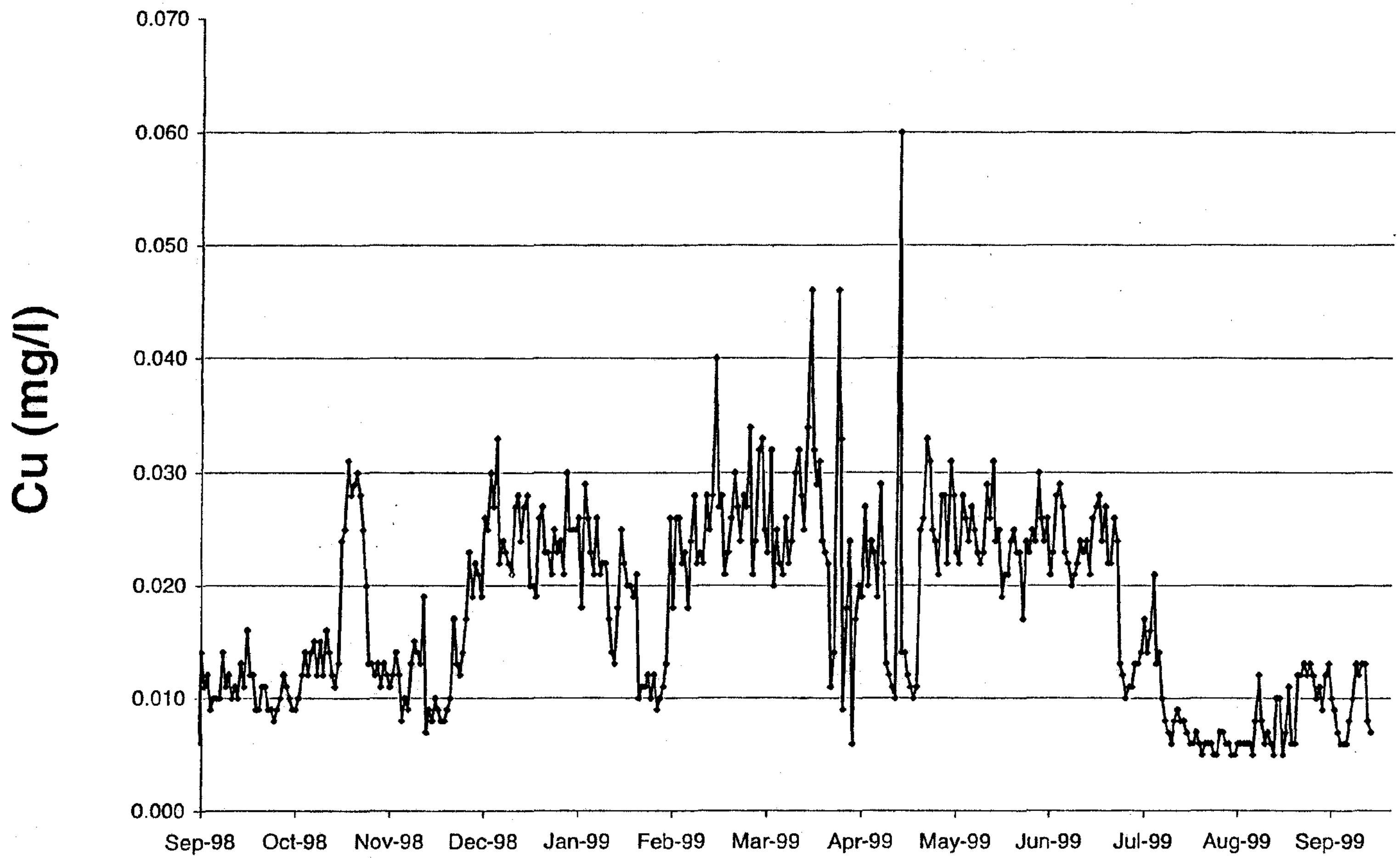
HANOVER PARK WRP EFFLUENT COPPER CONCENTRATION



METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

FIGURE 2

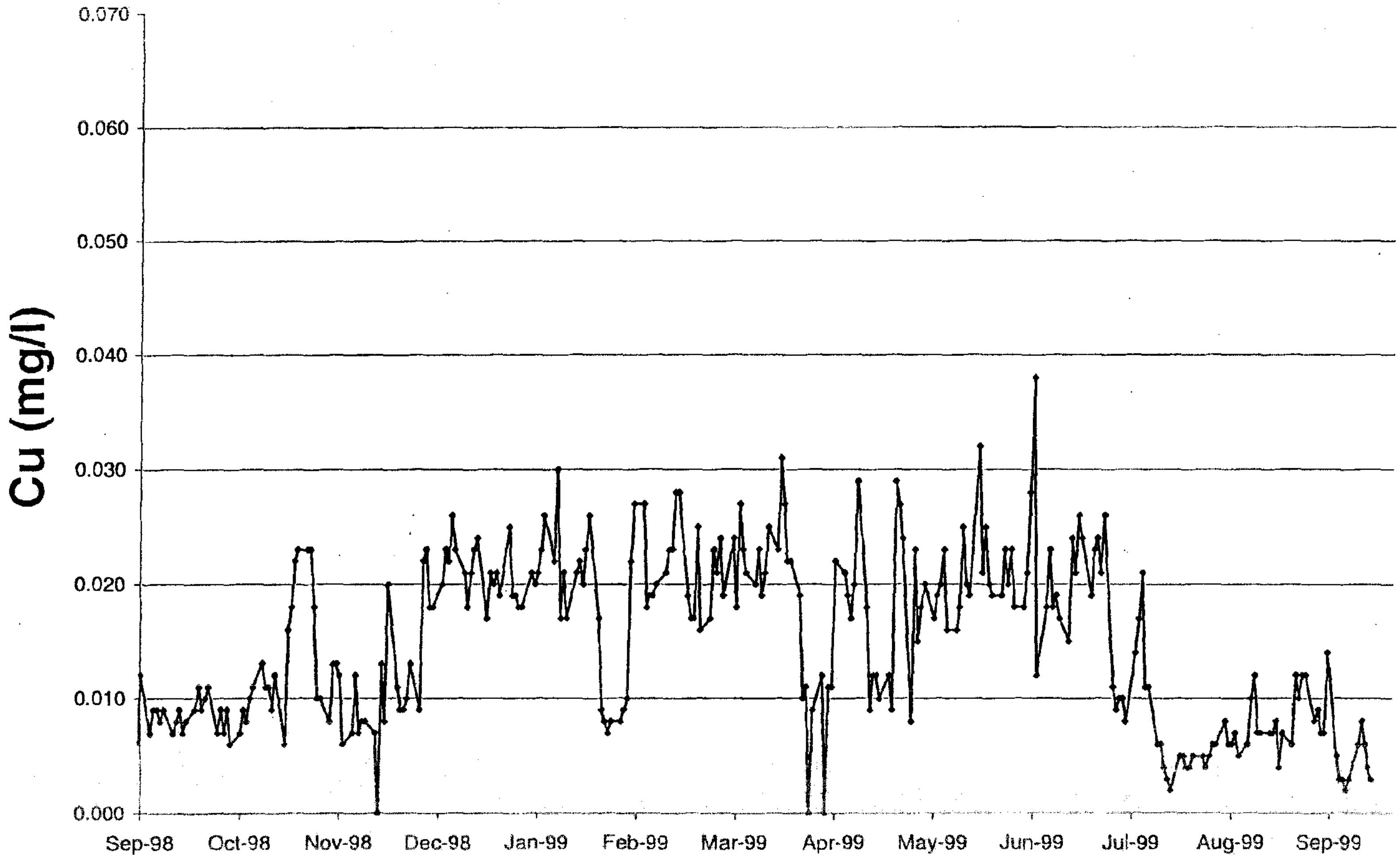
JOHN E. EGAN WRP EFFLUENT COPPER CONCENTRATION



METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

FIGURE 3

JAMES C. KIRIE WRP EFFLUENT COPPER CONCENTRATION



During the early part of 1998, the John E. Egan Laboratory installed a new inductively coupled plasma (ICP) instrument for the analysis of metals including copper. This instrument was evaluated and put on-line during June 1998. During December 1998, it was noticed that analysis of reference soil samples was giving low results. The methodology being employed at the time used yttrium as an internal standard to correct for nebulizer efficiency. It was determined that the soil samples contained yttrium, resulting in an overcorrection. The instrumentation was reprogrammed to skip the yttrium internal standard step. Whether this would cause an upward shift in the copper analytical results obtained with the wastewater samples was not known. The laboratory did a comparison in December 1999 of analyzing various plant wastewater samples with and without the internal standard, and found no substantial difference in the copper results.

A more detailed review of the analytical procedures for copper was undertaken by the Analytical Laboratory Division (ALD). The results of this review are presented in a memorandum dated June 15, 1999, to George R. Richardson from John Chavich (Appendix AI). Based upon this review, no apparent changes in the methodology which would affect the copper analysis were found.

In addition, a special study was carried out, by the ALD, in which grab samples of Hanover Park WRP effluent were collected and split among the three analytical laboratories at Calumet, John E. Egan, and Stickney WRPs. The grab samples were taken on six different days over the period of July 1 through 22, 1999. Split samples of these grab samples were analyzed by each laboratory, and the results are presented in Table 17. In general, the Calumet laboratory had the highest copper values, while the John E. Egan and Stickney laboratories had similar values for the same samples.

Decrease in Effluent Copper Concentration

As previously stated, a sudden decrease in final effluent copper concentrations occurred on July 8-9, 1999, during the special tertiary filter sampling. Similar decreases also occurred in effluent samples from the other north area WRPs served by the John E. Egan Laboratory. The suddenness and widespread change suggested that it may have been related to the analytical procedure, although the John E. Egan Laboratory reviewed their procedures and found no abrupt changes in any part of the analytical procedure with regard to calibration standards, instrument settings, personnel, etc. It is interesting that these lower effluent copper levels, which had

METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO

TABLE 17

HANOVER PARK WRP OUTFALL SPECIAL ROUND-ROBIN COPPER ANALYSIS

Sample Date	Laboratory	Total Copper, mg/L*
7/1/99	Calumet	**
	Egan	0.029
	Stickney	0.012
7/7/99	Calumet	0.031
	Egan	0.025
	Stickney	0.021
7/8/99	Calumet	0.023
	Egan	0.013
	Stickney	0.010
7/14/99	Calumet	0.021
	Egan	0.016
	Stickney	0.017***
7/21/99	Calumet	0.017
	Egan	0.011
	Stickney	0.012
7/22/99	Calumet	0.021
	Egan	0.010
	Stickney	0.028
Average	Calumet	0.023
	Egan	0.017
	Stickney	0.017

*Method detection limits for copper are as follows: Calumet - 0.01 mg/L, Egan - 0.002 mg/L, Stickney - 0.008 mg/L.
**Sample was not submitted to Calumet Laboratory; ICP was out of service.
***Value reported is from reanalysis on 7/23/99.

traditionally been found in the Hanover Park WRP effluent prior to the December 1998 through July 8, 1999 period, have continued through 1999.

Discussions with Hanover Park WRP operating personnel did not reveal any abrupt changes in operation during July 1999. A review of the copper data for the raw sewage did not show an observable decrease in concentration in July 1999. During the first eight days of July, the range of raw sewage copper was 0.057 to 0.149 mg/L. During the eight days after July 9, 1999, the values ranged from 0.089 to 0.120 mg/L. Since July 1999, raw sewage copper concentrations have remained within the typical range normally associated with the Hanover Park WRP influent.

To further evaluate possible causes of this sudden decrease in effluent copper values, the data at the other three north area WRPs were reviewed in more detail. All of the copper analyses for these WRPs are also carried out at the John E. Egan Laboratory. Figure 4 is a plot of the daily effluent copper values for each of the four WRPs during the month of July 1999. The daily values closely follow the same pattern at all four WRPs. All show the same sudden decrease in concentration occurring between July 8 and 10. This strongly suggests that the sudden decrease observed in the copper

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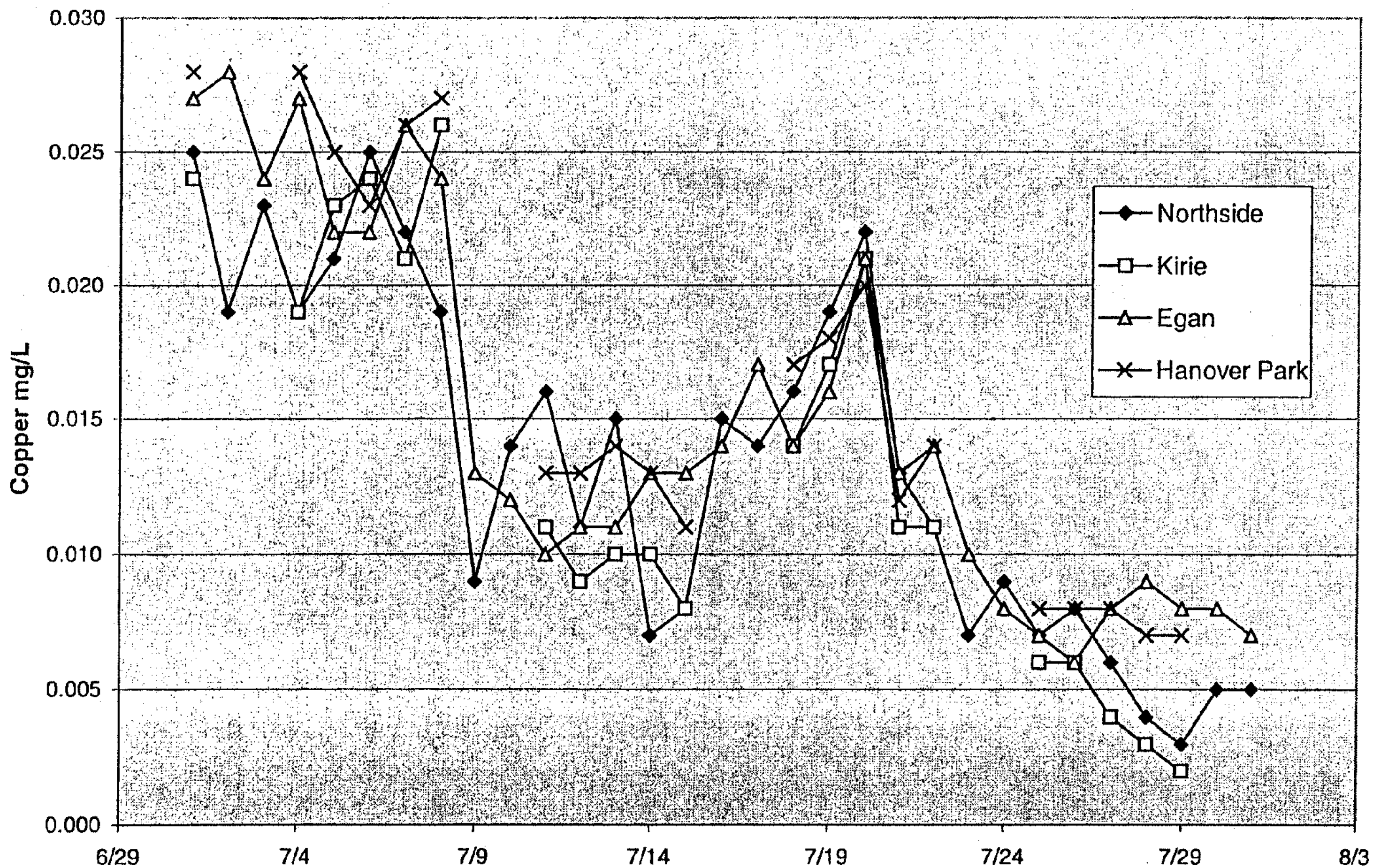
FIGURE 4

EFFLUENT COPPER VALUES AT THE NORTH AREA WRPS, JULY 1999



concentration of the Hanover Park WRP effluent was due to an analytical abnormality that occurred in the John E. Egan WRP analytical laboratory.

For this reason, it was requested that the R&D Department's Quality Assurance Coordinator review the analytical protocols for copper at the John E. Egan WRP, as well as the various correspondence provided by the ALD on this topic. The Quality Assurance Coordinator concluded, based upon the similarities in the copper variations in the samples from the three north area WRPs, that a bias error may have occurred in the copper analyses at the John E. Egan laboratory for samples with copper concentrations near the detection limit. Such a bias error may be caused by faulty background correction, poor calibration at low concentrations, improper matrix matching, or contamination of samples in the laboratory.

The Quality Assurance Coordinator also concluded that the laboratory "check" standards used as a quality control measure were out of range, and hence ineffective, because the concentration of the standard is too high relative to the low copper concentration that normally occurs in the Hanover Park WRP effluent. Further, the expected precision for low-level standards would be approximately ±0.002 mg/L based upon a minimum detection limit (MDL) study performed at the John E. Egan Laboratory on September 1, 1999, in which a 0.010 mg/L standard was analyzed seven times and showed an average recovery of 0.0102 mg/L (102.5 percent), with a range in recovery from 0.009 to 0.012 mg/L (91 to 117 percent). Thus, for low-level standards, the expected accuracy (deviation from true value) would also be about ±0.002 mg/L.

The recommendation of the Quality Assurance Coordinator was that a method blank and a low-level check standard be analyzed with each sample batch. These two control procedures are now being used at the John E. Egan Laboratory.

APPENDIX AI

MEMORANDUM FROM JOHN CHAVICH TO GEORGE RICHARDSON
DATED JUNE 15, 1999

INTEROFFICE MEMORANDUM

Metropolitan Water Reclamation District of Greater Chicago

DEPARTMENT: RESEARCH AND DEVELOPMENT DATE: June 15, 1999

TO: George Richardson
Analytical Laboratories
Division Coordinator

FROM: John Chavich

SUBJECT: Quality Assurance Data and Procedures for the Analysis of Copper at John Egan Analytical Laboratory

In anticipation of questions which may arise from the end users about the accuracy of copper data determined on the Perkin Elmer Optima 3200 ICP at the John Egan ALD, I would like to present a review of the QA data generated during the course of copper analysis on both liquid and solid matrices.

The quality assurance data generated for the liquid matrix samples analyzed for copper consists of accuracy, precision, and matrix spike recovery. The accuracy data is the percent recovery obtained on a Laboratory Control Standard (LCS) which is a standard made of a clean sample matrix (RO water) and a known quantity of analyte. The precision sample consists of a real sample and a replicate of the sample spaced at least five samples apart. The two values are used by LIMS to calculate a normalized precision. A weekly matrix spike is also run on a selected matrix and the percent recovery is also determined.

The liquid matrix QA data that we have obtained during the months of April through June of 1999 is shown on the attached graphs A, B, and C. The accuracy graph, A, during the period of May through June shows that the percent recoveries obtained on the LCS standard analyzed with each batch of samples have been well within the ICP specification limits of 110% to 90%. The average percent recovery is 99.81% which is within the 95% to 105% range for the average recovery criteria established by the QA coordinator. The precision graph, B, illustrates that the normalized precision has a range of +0.04 to -0.08 with an average signed precision of -0.02. The criteria for acceptable normalized precision range is +0.15 to -0.15 and the average signed precision criteria is +0.05 to -0.05. The precision data meets these criteria. A matrix spike sample is analyzed one time per week, and the percent recovery is shown on graph C for the period of June 1998 to June 1999. The range was greater in 1998 due to the fact that the instrument had gone on line in May of 1998. The data obtained

SUBJECT: Quality Assurance Data and Procedures for the Analysis of Copper at John Egan Analytical Laboratory

in 1999 has been in the range of 100% to 94% with an average matrix spike recovery of 100.24%.

The quality assurance data generated for the solid matrix samples analyzed for copper consists of the same LCS standard used for the liquid matrix accuracy. In addition, an accuracy standard is made from a certified sewage sludge sample manufactured by Environmental Resource Associates (ERA). This sample is digested and analyzed along with the north area 503 sludge metal samples being analyzed. This way the digestion process as well as the analysis process can be monitored for process control. Looking at the attached graph D for the period of March 1999 when the program was started to June 1999 the percent recoveries have been in the range of 110% to 98% with an average recovery of 104.24%. The performance acceptance limits published by ERA for this sample are 128.9% to 70.95%. The certified value for copper for this sample is 661 mg/Kg. We also prepare another graph, E, for normalized precision for copper in solid matrix samples. For the months of April through June of 1999, the normalized precision for sludge samples has a range of +0.02 to -0.04 and a signed, average normalized precision of -0.01. These values all meet the acceptance criteria for precision in the District's QA program.

To further verify copper analytical data, a separate aliquot from the shelf sample will be analyzed for any Hanover Park outfall sample having a copper value greater than 0.027 mg/L.

John Chavich

John Chavich
Sanitary Chemist IV

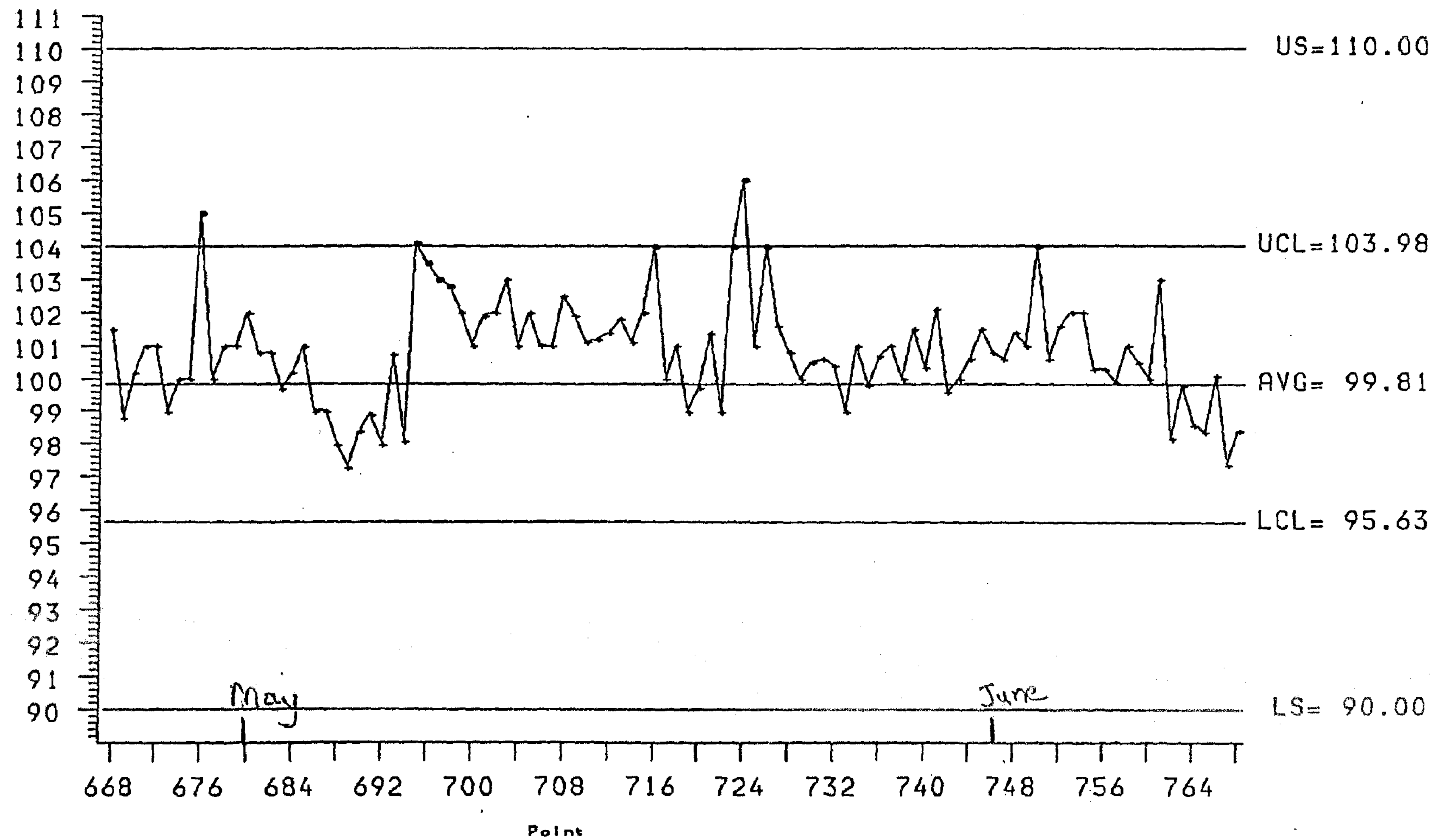
JC:gh
Attachments

Graph A

MVRDGC Control Charts

Name of Chart	: JE_CU1	Date of Plot	: 10-JUN-1999 17:35		
Limits Type Indiv	: Specified	Limits Type MR	: Date	Spec Limits	: Specified
Trend Table Indiv	: DAC				
Analysis	: MET_PL	Component	: Cu		

Individual Chart



Graph B

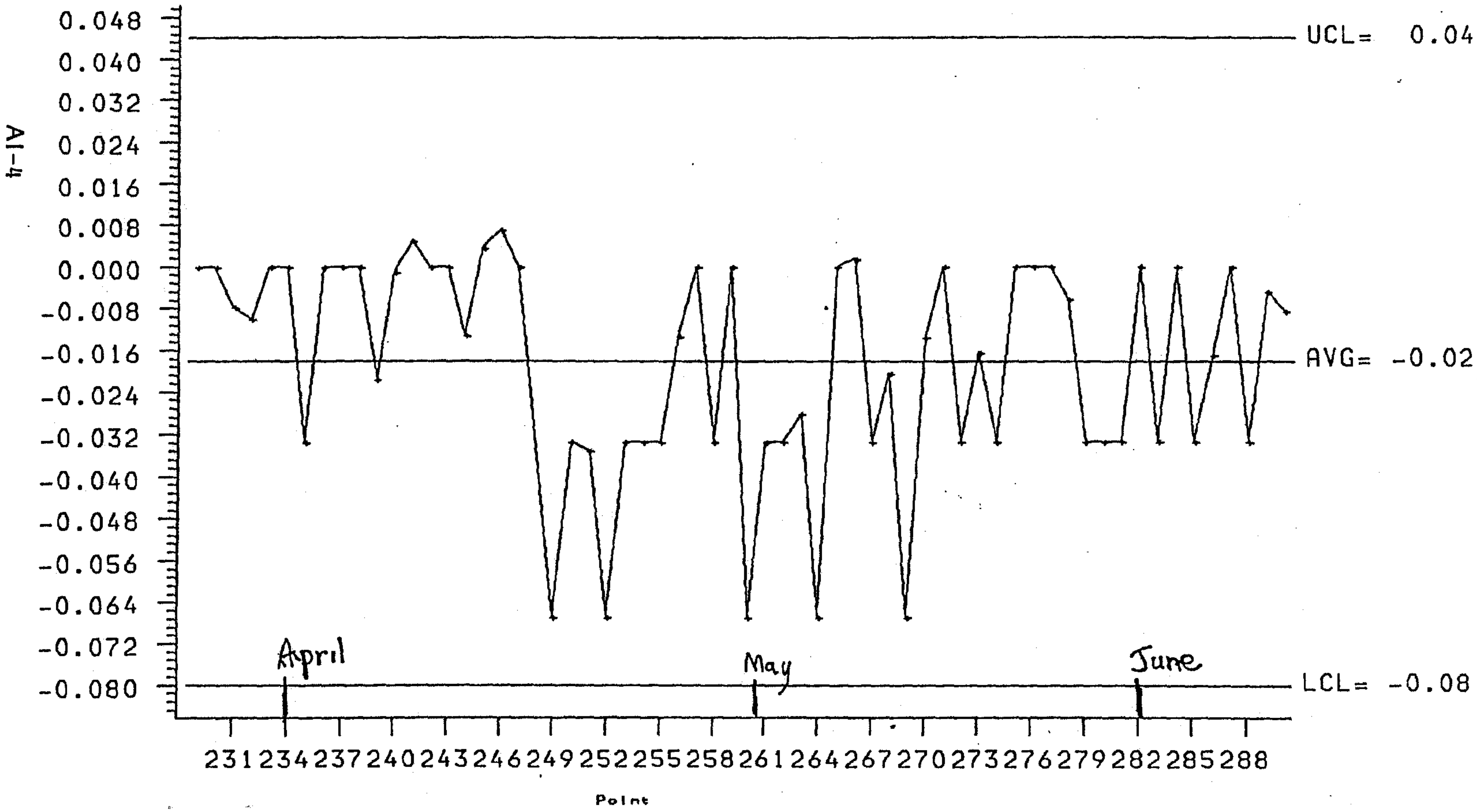
MWRDGC Control Charts

Name of Chart . JE_CUP1
Limits Type Indiv . Specified
Analysis . MET_PL

Date of Plot . 10-JUN-1999 17:44
Limits Type MR . Data
Component . Cu

Spec Limits . Specified

Individual Chart



Graph C

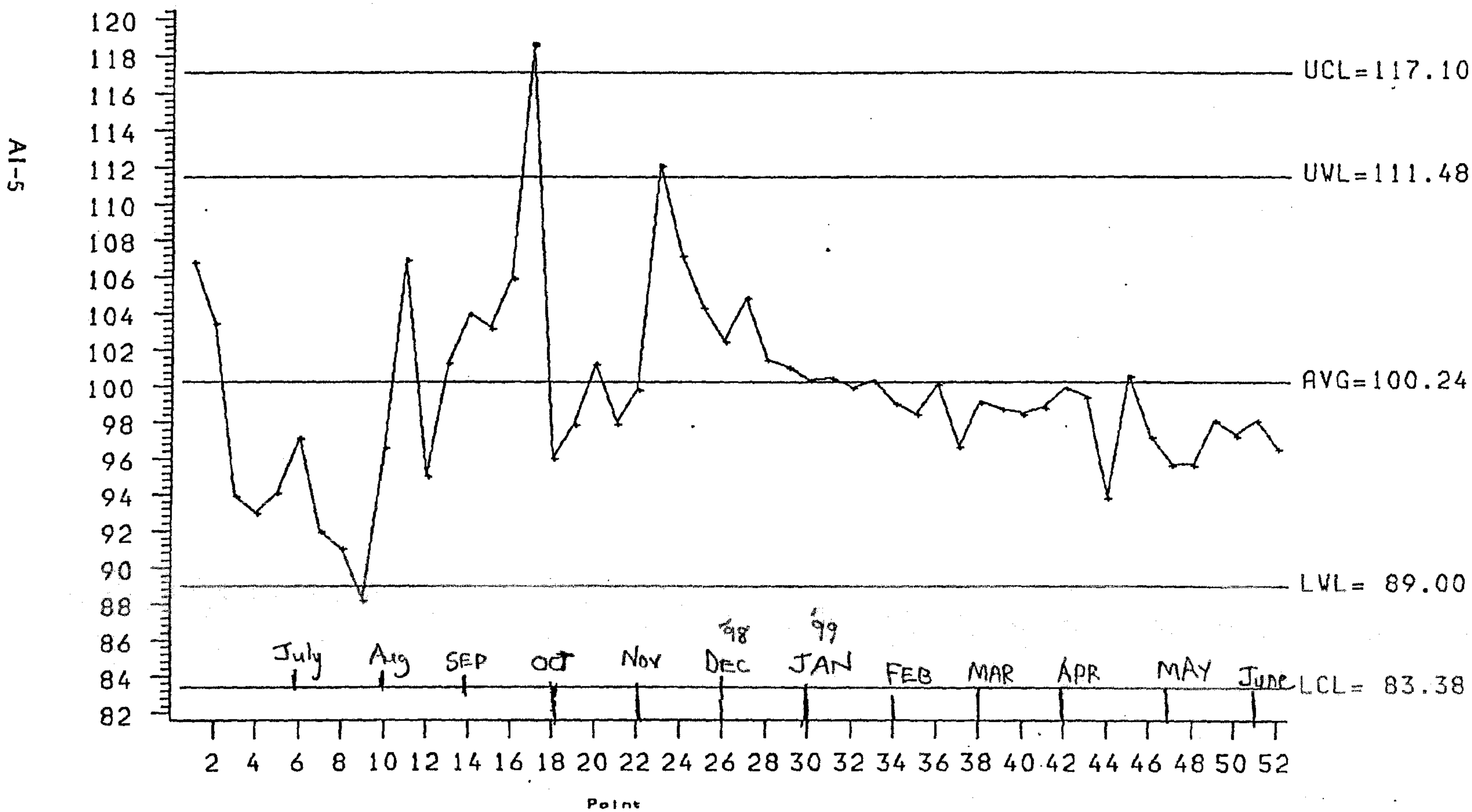
MVRDGC Control Charts

Name of Chart : JE_CUSP1
Limits Type Indiv : Specified
Trend Table Indiv : QAC
Analysis : MET_PL

Date of Plot : 10-JUN-1999 17:47
Limits Type MR : Date
Component : Cu

Spec Limits : Specified

Individual Chart



AI-6

Graph D

MVRDGC Control Charts

Name of Chart	: JERA_CU1	Date of Plot	: 10-JUN-1999 17:52				
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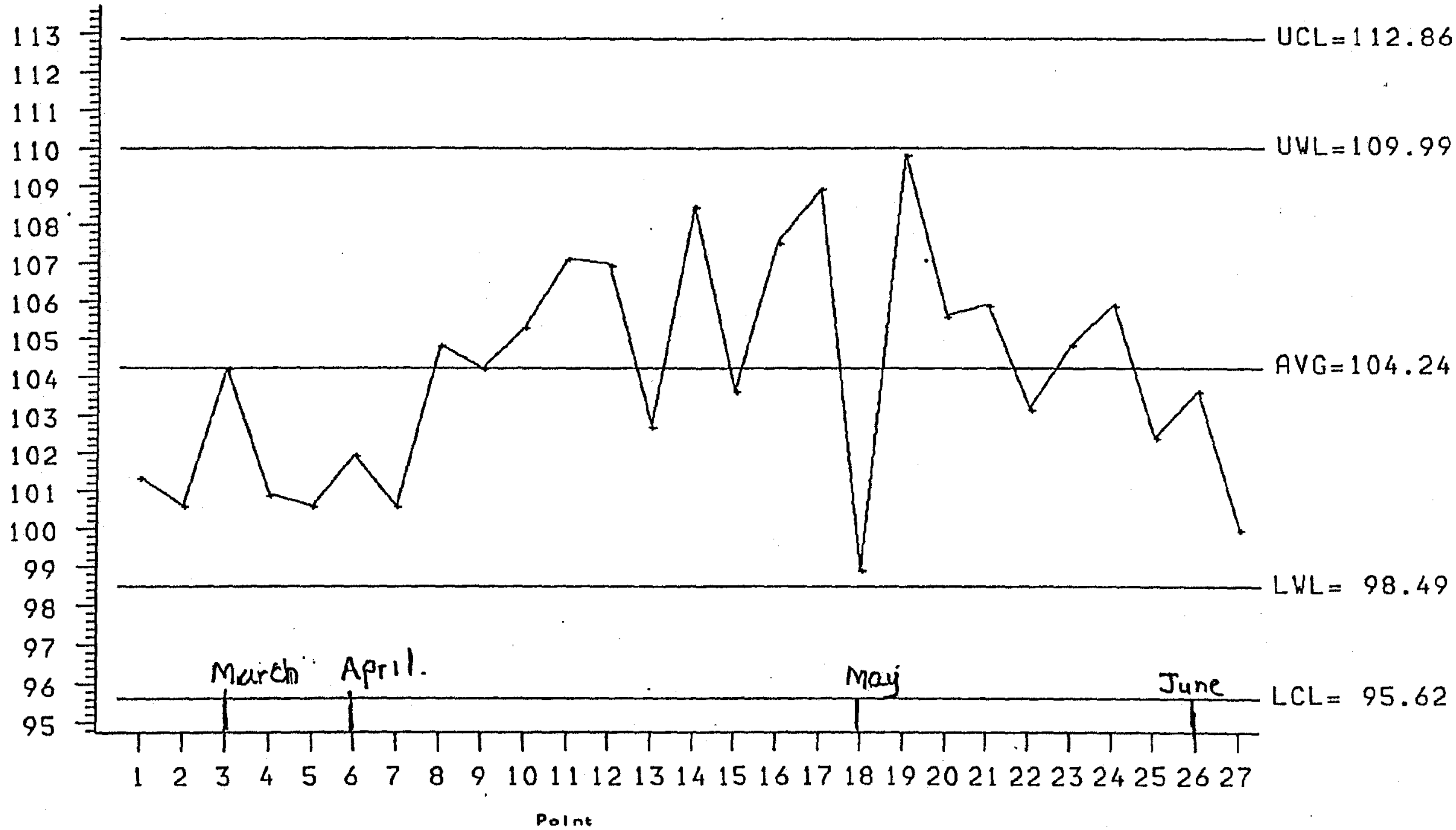
Trend Table Indiv	: QAC						
Analysis	: MET_SPL	Component	: Cu				

Individual Chart



Graph E

MVRDGC Control Charts

Name of Chart	: JE_CUSLP1	Date of Plot	: 10-JUN-1999 17:56		
Limits Type Indiv	: Specified	Limits Type MR	: Date	Spec Limits	: Specified
Trend Table Indiv	: QAC				
Analysis	: MET_SPL	Component	: Cu		

Individual Chart