OUTFALL K-018 TRC INVESTIGATION FINAL REPORT (U)

by

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Savannah River Site
Aiken, South Carolina 29808

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Chlorine

**OUTFALL K-018
TRC INVESTIGATION
FINAL REPORT**

By

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EXECUTIVE SUMMARY

During 1993, seven (7) different samples taken at Reactor Outfall K-018 for Total Residual Chlorine exceeded the permitted requirement for the outfall of <0.1 mg/L. Following the second exceedance, a Mitigation Action Plan was issued to investigate and identify the cause of the exceedances. The following potential causes were identified:

1. Unauthorized/unknown operational discharge
2. Upstream industrial discharge to the Savannah River prior to SRS usage
3. Sanitary Waste Treatment Plant discharge
4. Sampling Methodology
5. Naturally occurring river water interference

Of these possibilities, it was determined that naturally occurring river water interference was the most likely cause and an in-depth sampling program, outlined in a Program Action Plan, was initiated to complete the investigation. The investigation determined that oxidized manganese present in the river water prior to usage within K-Area causes a false high reading for Total Residual Chlorine. It is this presence of the manganese interference, not operational discharge, that caused the exceedances at Outfall K-018.

1.0 INTRODUCTION

Reactor Operations is presently permitted to discharge wastewater to Outfall K-018 that includes K-Reactor Cooling Tower blowdown, 186-Basin overflow, neutralization wastewater (intermittently from Power Operations), as well as miscellaneous 105-K Building wastewater (Reference 1). In addition, the K-Area Sanitary Waste Treatment Plant (SWTP) wastewater is discharged to the outfall after treatment with sodium hypochlorite. The Environmental Monitoring Section (EMS) analyzes effluents to Outfall K-018 for Total Residual Chlorine (TRC) with a standard residual chlorine method (Reference 2) utilizing the Hach DR100 Colorimeter field unit. (Note: Since the completion of the study, EMS has switched to using the Hach Pocket Colorimeter with digital readout). Samples are analyzed twice per week per the requirements of NPDES Permit #SC0044903. The limit for TRC per SCDHEC regulations is 0.011 mg/L, however, because this is below the present state approved calibrated detection limit of 0.1 mg/L, the current limit at the K-018 Outfall is <0.1 mg/L.

On seven different occasions during 1993, samples taken at the K-018 Outfall for TRC exceeded the permitted requirement of <0.1 mg/L, ranging from 0.1 - 0.18 mg/L. Table 1 summarizes these results. On 7/26/93, following the second exceedance, a Mitigation Action Plan (Reference 3) was issued to outline a plan to investigate and identify the cause of the exceedances. After the additional five exceedances had occurred, an update to the original MAP (Reference 4) was issued, followed by a Program Action Plan (Reference 5). The PAP outlined an in-depth sampling program to determine the extent to which river water contributed to the exceedances due to interferences in the water.

This final report, as required by the PAP, summarizes the findings of the sampling study as well as all other significant actions completed to date for the determination of the cause of the TRC exceedances at Outfall K-018.

2.0 INVESTIGATION OF CAUSES

Because of reduced operations in K-Area, there are no systems operating (other than the SWTP) that could discharge chlorine to the outfall, and, at the times of the exceedances, there were no process upsets or spills documented that would have discharged chlorine. Because of the length that an upstream industrial discharge would have to travel to reach K-Area it is very unlikely that enough residual chlorine would be in the river water for it to be considered as a source. Thus, the most likely cause of the exceedances was from either the SWTP discharge, problems with the sampling methodology, or naturally occurring river water interference.

2.1 Chlorine Sources - SWTP

Sodium hypochlorite (NaOCl) is used to disinfect SWTP wastewater prior to discharge. Normally, the hypochlorite (10.5% NaOCl) is fed at a rate of approximately 4 ml/min, along with 2 gpm of domestic water, to a 510 gallon chlorine contact chamber where it is mixed with the SWTP wastewater. The hypochlorite solution is a constant feed and at times of low volume usage of the SWTP (weekends, holidays, off-shifts, etc.) it will continue flowing into the contact chamber even though no wastewater is flowing to the chamber. When wastewater flow resumes, the chlorine is discharged in a slug to the outfall.

At the above feed rates, assuming no contact with wastewater, it was determined that a maximum concentration of 31 mg/L TRC could be detected in the chamber under normal operating conditions (Reference 6). During the PAP sampling study (Section 3.1), SWTP discharges were found as high as 64.5 mg/L TRC. This was due to operators increasing the hypochlorite feed rate after TRC readings on 10/12 and 10/13 indicated that TRC was too low to adequately disinfect the wastewater.

Calculations were also done to determine TRC results after the SWTP discharge was mixed with the 186-basin overflow prior to release to the K-018 Outfall (Reference 7). Using the conditions from above, SWTP flow of 17 gpm, 186-Basin flow rates of 5,000 gpm, 8,000 gpm and 11,000 gpm, respectively, and assuming a 186-Basin TRC concentration of 0.04 mg/L, TRC results upon mixing would be 0.146 mg/L, 0.106 mg/L and 0.088 mg/L. This indicates that even after mixing, a potential for high TRC results exists. However, because the mixed discharge travels approximately one mile through open channels to the K-018 sampling point, it is highly unlikely that any TRC as a result of SWTP discharge would still be present. Even so, Site Services Engineering (SSE) has taken steps to ensure that hypochlorite feed is kept as low as possible without affecting disinfection capabilities. A flow-weighted feed system will be installed at the K-Area SWTP in 1994 to ensure that hypochlorite is only fed when needed by the system. Additionally, ultra-violet light disinfection systems are planned to be installed in 1995 to replace all chlorine treatment systems on site.

2.2 Methodology

Because no operational cause of the exceedances could be specifically determined, the investigation also examined the methodology used for TRC analysis. The method used is the DPD Colorimetric Method (Reference 2) utilizing a Hach field colorimeter. Although laboratory conditions can set detection limits as low as 0.01 mg/L, a field measurement detection limit of 0.1 (per SCDHEC) ± 0.04 mg/L is used. The method consists of preparation of standards in the range of 0.1 mg/L (0.05 mg/L for the sampling study) to 2.0 mg/L, instrument calibration and field analysis.

Because of the number of steps required by SCDHEC for standards preparation and the accuracy of measurements required therein, this method is susceptible to human error. This was verified during the sampling study in that many of the TRC readings had to be adjusted by as much as

+0.05 mg/L (see Figures 2-8) to account for calibration. Additionally, the EPA has cited a relative error for this procedure to be 15.6% (Reference 8).

Although human error is a factor when using this methodology, it is the preferred method because of its low detection limit (Reference 9). In further discussions with EMS and SSE personnel, it was determined that the DPD Colorimetric Method using a Hach field colorimeter is considered the Best Available Technology (BAT) for field use in TRC determinations.

2.3 Interferences

Since the DPD Colorimetric Method for TRC was determined to be the BAT, the investigation then centered on interferences in river water as the cause of the TRC exceedances. The DPD Method identifies oxidized manganese, chromium, copper (among others) as possible interferences with TRC analysis. A two-week sampling program was initiated by EMS to sample for TRC at seven different locations leading to the K-018 Outfall as well as the outfall itself (see Figure 1). Baseline sampling for the above interferences was completed (except for the SWTP) and interference sampling at the time that any TRC levels of ≥ 0.1 mg/L were found was also done. Results of all the sampling can be found in Tables 2 and 3 (Reference 10). As can be seen, various levels of manganese are present at all sites. Further discussion of the chlorine and interference sampling results and their significance is found in Section 3.0.

3.0 SAMPLING RESULTS

3.1 Total Residual Chlorine

During the period of 10/11/93 through 10/24/93, EMS conducted TRC surveys at the following locations (see Figure 1):

1. Influent to 186-K Basin
2. 186-K Basin
3. SWTP at Outfall K-012
4. 107-K Building Effluent
5. 105-K Chiller Unit Cooling Water Discharge
6. Discharge at Headwall to K-Canal
7. Indian grave Branch Station IGB-21
8. Outfall K-018

The purpose of the sampling was to verify sources of TRC. Results are found in Table 2. During the two-week period, a total of ten occurrences (not including SWTP discharge) of TRC ≥ 0.1 mg/L were recorded. Five times, the TRC was high in the 186-K Basin influent, which is pumped directly from the Savannah River and receives no chemical treatment onsite. On four occasions, high TRC was found in areas fed by the 186-K Basin (twice in the basin, once at the 107 Building, and once in the Chiller Unit cooling water) which again, receives no chemical treatment. The final occurrence was at the headwall to the K-Canal, after all operational sources have been mixed together. The SWTP discharge ranged from 0.2 - 64.5 mg/L during the study, which verified it as a potential source, although as previously discussed, there is no apparent relationship believed between high TRC at the SWTP and high TRC at the K-018 Outfall.

3.2 Interferences

Along with a set of baseline samples, interference sampling was completed at each occurrence of TRC ≥ 0.1 mg/L. Results are found in Table 3. While chromium and copper were generally less than detectable, manganese levels were found in all cases and ranged from 0.02 - 0.34 mg/L.

The SSE performed an additional study using sodium arsenite as a reagent to measure oxidized manganese after taking the initial TRC reading. The measurement after the arsenite is added is subtracted from the initial reading to give the actual TRC level. Samples were taken at the 186-K Basin and at the K-018 Outfall. Results are shown in Table 4. All of the readings for TRC were within 0 ± 0.03 mg/L, taken on the Hach DR100 Colorimeter, which has an accuracy of ± 0.04 mg/L. This strongly suggests that the TRC exceedances are explicitly caused by interferences found in the river water rather than operational discharge.

3.3 Interference Removal Methods

EMS is currently reviewing different methods to use for interference removal, including use of sodium arsenite, sulfamic acid, sodium thiosulfate and sodium sulfite. Sodium arsenite and sulfamic acid are listed carcinogens and are not the most desirable to handle. Sodium thiosulfate and sodium sulfite are actual dechlorinating agents which may also remove the interferences in addition to the chlorine. A recommendation will be made by EMS as to which method is best suited for site application.

4.0 CONCLUSIONS

The cause of the TRC exceedances at Outfall K-018 is from interferences with the DPD Colorimetric Method found in the river water, specifically, from oxidized manganese. Although the SWTP is a known source of elevated TRC, it was clearly demonstrated that it, alone, could not be the source of the high TRC at Outfall K-018. The steps being taken by SSE to reduce TRC discharge will be completed as scheduled, however, to help ensure that discharge of chlorine is kept as low as possible. Though it has been shown that some error is to be expected with the current method used for TRC analysis, it is not recommended that the method be changed, as the use of the DPD Colorimetric Method is the proven BAT. The use of an approved method for interference removal, as cited in the DPD method, however, should be incorporated into site procedures. Presently, the K-018 Outfall is the only outfall on site with a requirement to monitor for TRC. However, because of evolving regulations concerning environmental toxicity, it is expected that all site outfalls will have TRC monitoring requirements in the near future. Because of this, the findings of this report should be used to assist in future permitting compliance with SCDHEC regulations. Additionally, the findings of this investigation will restore the site's ability to realize goals for NPDES permit compliance.

5.0 REFERENCES

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4. RRD-RES-930202, Outfall K-018 TRC Mitigation Plan Update, 10/5/93.
5. RRD-RES-930205, Program Action Plan For Outfall K-018 TRC Mitigation Plan, 10/15/93.
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9. ESH-ESS-93-0557, Audit Report - National Pollutant Discharge Elimination System (NPDES) SC0044903 Outfall K-018: Report Number 07-02-93-0027, 10/6/93.
10. Memo, Eldridge to Skiff, K-018 TRC Study Report, 11/18/93.

6.0 ATTACHMENTS

6.1 List of Figures

1. K-Area TRC Sample Study Locations
2. TRC Calibrated vs Field Readings, 186-Basin Influent
3. TRC Calibrated vs Field Readings, 186-Basin
4. TRC Calibrated vs Field Readings, 107-K Effluent
5. TRC Calibrated vs Field Readings, Chiller Unit CW
6. TRC Calibrated vs Field Readings, K-Canal Headwall
7. TRC Calibrated vs Field Readings, Indian Grave Branch
8. TRC Calibrated vs Field Readings, K-018 Outfall

FIGURE 1
K-AREA TRC SAMPLE STUDY LOCATIONS

1. Influent to 186-K Basin
2. 186-K Basin
3. SWTP at Outfall K-012
4. 107-K Building Effluent
5. 105-K Chiller Unit Cooling Water Discharge
6. Discharge at Headwall to K-Canal
7. Indian Grave Branch Station IGB-21
8. Outfall K-018

FIGURE 2
TRC CALIBRATED vs FIELD READINGS
186-K BASIN INFLUENT

FIGURE 3
TRC CALIBRATED vs FIELD READINGS
186-K BASIN

FIGURE 4
TRC CALIBRATED vs FIELD READINGS
107-K EFFLUENT

FIGURE 5
TRC CALIBRATED vs FIELD READINGS
CHILLER UNIT CW

FIGURE 6
TRC CALIBRATED vs FIELD READINGS
K-CANAL HEADWALL

FIGURE 7
TRC CALIBRATED vs FIELD READINGS
INDIAN GRAVE BRANCH

FIGURE 8
TRC CALIBRATED vs FIELD READINGS
K-018 OUTFALL

6.2 List of Tables

1. Outfall K-018 TRC Exceedance Results - 1993
2. TRC Sample Study Results
3. TRC Interference Study Results
4. SSE Interference Removal Sampling Results

TABLE 1
OUTFALL K-018 TRC EXCEEDANCE RESULTS - 1993

<u>DATE</u>	<u>RESULT</u>
1/5/93	0.16 mg/L
6/14/93	0.18 mg/L
9/1/93	0.1 mg/L
9/7/93	0.1 mg/L
9/21/93	0.11 mg/L
9/28/93	0.13 mg/L
10/4/93	0.1 mg/L

TABLE 2
TRC SAMPLE STUDY RESULTS

DATE	10/11/93				10/12/93				10/13/93				10/14/93			
	Time	pH	Temp	TRC	Time	pH	Temp	TRC	Time	pH	Temp	TRC	Time	pH	Temp	TRC
SWTP	1350	8.0	20.6	0.25	1005	7.1	20.0	0.20	944	6.9	19.0	0.20	1000	8.1	20.0	0.20
107 EFFLUENT	1400	6.2	20.0	0.04	950	5.7	21.0	0.02	1005	6.8	21.0	0.03	940	6.4	22.0	0.02
CHILLER CW	1445	6.0	21.0	0.02	955	6.3	21.0	0.02	1005	6.6	21.0	0.02	940	6.4	22.0	0.03
186-BASIN	1510	5.8	21.0	0.04	1020	5.7	21.0	0.04	1030	6.7	20.0	0.02	1020	6.6	19.0	0.05
186 INFLUENT													1030	6.4	18.5	0.02
K-018	1525	6.2	20.0	0.06	1120	6.8	21.0	0.07	1120	6.8	20.0	0.03	1120	6.7	19.5	0.03
IGB-21	1535	5.2	18.0	0.02	1040	6.8	17.0	0.05	1050	6.8	17.0	0.02	1050	6.1	14.0	0.02
K-CANAL	1535	6.1	19.5	0.03	1100	7.0	21.0	0.05	1100	6.9	20.0	0.04	1100	6.7	20.0	0.04
	10/15/93				10/16/93				10/17/93				10/18/93			
	Time	pH	Temp	TRC	Time	pH	Temp	TRC	Time	pH	Temp	TRC	Time	pH	Temp	TRC
SWTP	940	8.1	21.0	1.50	935	10.1	21.0	15.00	940	10.3	21.5	64.30	950		23.0	25.00
107 EFFLUENT	1000	7.1	21.0	0.03	950	6.3	22.5	0.06	950	7.9	21.5	0.07	1030	7.8	24.0	0.09
CHILLER CW	1005	6.8	21.0	0.03	1000	6.2	19.0	0.05	950	6.6	21.5	0.06	1040	6.6	19.0	0.06
186-BASIN	1020	6.6	20.0	0.03	1015	6.0	19.5	0.05	1015	6.5	20.0	0.07	1100	6.8	20.5	0.11
186 INFLUENT	1020	6.5	19.0	0.04	1030	5.9	19.5	0.05	1020	6.5	20.0	0.07	1105	6.7	20.5	0.10
K-018	1107	6.9	20.0	0.04	1110	6.4	20.0	0.06	1105	6.8	20.0	0.08	1130	6.6	20.5	0.09
IGB-21	1043	6.0	17.0	0.03	1050	5.4	18.0	0.05	1035	6.2	19.0	0.07	1205	6.3	19.0	0.09
K-CANAL	1055	6.9	19.5	0.05	1100	6.3	20.0	0.05	1055	6.8	20.0	0.07	1140	7.0	21.0	0.14
	10/19/93				10/20/93				10/21/93				10/22/93			
	Time	pH	Temp	TRC	Time	pH	Temp	TRC	Time	pH	Temp	TRC	Time	pH	Temp	TRC
SWTP	940		24.0	0.83	1010	7.8	24.0	0.79	1010	7.7	24.0	1.25	1230	7.5	24.0	0.72
107 EFFLUENT	1000	7.6	21.0	0.05	1030	6.7	26.0	0.06	950	6.9	24.0	0.05	1235	6.8	23.0	0.05
CHILLER CW	1000	7.2	26.0	0.06	1040	6.3	22.0	0.09	955	6.5	23.0	0.10	1240	6.2	22.0	0.05
186-BASIN	1020	7.5	21.0	0.08	1050	6.5	22.0	0.07	1040	6.8	22.0	0.06	1250	6.5	21.0	0.06
186 INFLUENT	1020	7.5	21.5	0.09	1100	6.5	22.0	0.10	1045	6.8	22.0	0.06	1250	6.2	21.0	0.14
K-018	1105	6.1	21.0	0.06	1200	6.4	22.0	0.09	1130	7.0	22.0	0.09	1345	6.4	20.0	0.06
IGB-21	1040	7.5	19.0	0.05	1125	5.8	21.0	0.06	1110	6.3	22.0	0.04	1320	5.7	20.0	0.05
K-CANAL	1055	5.9	21.0	0.07	1145	6.3	22.0	0.09	1120	6.8	22.0	0.06	1330	6.5	21.0	0.05
	10/23/93				10/24/93											
	Time	pH	Temp	TRC	Time	pH	Temp	TRC								
SWTP	950	8.4	20.0	13.20	910	8.3	20.0	27.50								
107 EFFLUENT	1005	5.5	22.0	0.10	935	7.3	22.0	0.00								
CHILLER CW	1010	7.0	15.5	0.00	940	6.0	20.0	0.05								
186-BASIN	1030	7.2	20.5	0.07	950	6.1	19.5	0.10								
186 INFLUENT	1040	6.6	20.5	0.13	955	5.7	19.0	0.11								
K-018	1130	7.2	20.0	0.06	1055	6.4	19.5	0.06								
IGB-21	1110	6.6	17.0	0.05	1025	5.5	16.0	0.00								
K-CANAL	1125	7.1	21.0	0.07	1035	6.4	19.5	0.07								

TABLE 3
TRC INTERFERENCE STUDY RESULTS

LOCATION	DATE	TIME	TRC mg/L	Cr mg/L	Cu mg/L	Mg mg/L	Mn mg/L
K-018	10/11/93	1520	0.06	<0.02	<0.01	1.210	0.0291
186-BASIN	10/12/93	1020	0.04	<0.02	<0.01	1.260	0.0499
IGB-21	10/12/93	1040	0.05	<0.02	<0.01	0.815	0.0696
K-CANAL	10/12/93	1100	0.08	<0.02	<0.01	1.270	0.0532
186-BASIN	10/18/93	1100	0.11	<0.02	<0.01	1.250	0.0457
K-CANAL	10/18/93	1140	0.10	<0.02	<0.01	1.300	0.0474
186 INFLUENT	10/18/93	1105	0.10	<0.02	<0.01	1.240	0.0755
K-018	10/20/93	1200	0.09	<0.02	<0.01	1.240	0.0243
186 INFLUENT	10/20/93	1100	0.10	<0.02	<0.01	1.250	0.0767
CHILLER CW	10/21/93	1000	0.10	<0.02	3.73	1.420	0.3400
186 INFLUENT	10/22/93	1250	0.14	<0.02	<0.01	1.300	0.0691
107 EFFLUENT	10/23/93	1020	0.10	<0.02	0.052	0.562	0.0747
186 INFLUENT	10/23/93	1045	0.10	<0.02	<0.01	1.310	0.0791
186 BASIN	10/24/93	950	0.10	<0.02	<0.01	1.280	0.0431
186 INFLUENT	10/24/93	955	0.11	<0.02	<0.01	1.340	0.0962

TABLE 4

SSE INTERFERENCE REMOVAL SAMPLING RESULTS (mg/L)

186-K Basin	Date	TRC Standard	TRC From Mn Only	Actual TRC
	11/3/93	0.12	0.09	0.03
	11/4/93	0.07	0.10	-0.03
	11/5/93	0.04	0.05	-0.01
	11/8/93	0.04	0.02	0.02
	11/9/93	0.02	0.02	0.00
	11/10/93	0.06	0.04	0.02
	11/11/93	0.05	0.04	0.01
K-018 Outfall	11/10/93	0.05	0.02	0.03
	11/11/93	0.04	0.02	0.02
	11/12/93	0.07	0.04	0.03
	11/15/93	0.06	0.06	0.00
	11/16/93	0.04	0.07	-0.03
	11/17/93	0.06	0.04	0.02
	11/18/93	0.03	0.03	0.00

END

DATE

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