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DECHLORINATION WITH SULFUR DIOXIDE BEFORE ADSORPTION: DESIGN, OPERATION AND PERFORMANCE OF A PILOT-SCALE SYSTEM

Joan H. Kaczmarczyk
Senior Sanitary Chemist

Eugene Shpirt, PhD
Research Scientist

Katherine T. Alben, PhD
Research Scientist

Wadsworth Center for Laboratories and Research
New York State Department of Health
Empire State Plaza
Albany, NY 12201-0509

INTRODUCTION

Sulfur dioxide (SO_2) is an interesting reagent for water quality research projects, because it is commonly used in full-scale drinking-water treatment. Traditionally, SO_2 has been added for dechlorination. More recently, SO_2 and related compounds in the S(IV) oxidation state have been shown to significantly reduce concentrations of mutagenic disinfection by-products in chlorinated natural waters (1). For this project, SO_2 was used for dechlorination to inhibit the formation of surface oxides on a granular activated carbon (GAC) pilot column, which can potentially reduce adsorption capacities for organics.

In a pilot-scale system, SO_2 has the advantage of being easy to deliver from gas cylinders. Many of the alternative S(IV) compounds have the disadvantage of being solids, which have to be pre-mixed in batch solutions. In general, these alternatives to SO_2 are also more expensive. However, low gas flows are required for pilot-scale systems using SO_2, and low flows are difficult to regulate with a minimum of expense. This presentation describes the design and performance of a dechlorination system using SO_2 that was interfaced to a GAC pilot-column system and kept in operation for 30 weeks at the Waterford Water Works, Waterford, NY.

EXPERIMENTAL METHODS

Flow System for GAC Pilot Columns and Dechlorination Using SO_2 Figure 1 shows the flow path for influent to three GAC pilot columns operated in parallel. Pilot column 1 was operated using chlorinated influent and served as a control for pilot columns 2 and 3. Pilot column 2 was used to study GAC performance in response to simulated chemical spills: select results are described elsewhere in this volume (2). Pilot column 3 was operated using dechlorinated influent. Operating conditions for the pilot columns and dechlorination system are summarized in Table 1. Finished Waterford drinking water was used as the supply for the pilot-column system, after all stages of physical-chemical treatment: aeration; coagulation (alum, activated silica, powdered activated carbon); prechlorination; flocculation; sedimentation; filtration; post-chlorination; pH adjustment (sodium bicarbonate); fluoridation. The Waterford Water Works, pilot-column design and operation are described in detail elsewhere (3).

A schematic for the 3 GAC pilot columns is given in Figure 2, indicating the location of valves to regulate water pressures and flow as well as valves for collecting water and GAC samples. Reservoirs for chemical feed were connected only to pilot column 2. Solenoids 4, 5 and 6 were used to shut off effluent from pilot columns 1,2 and 3 respectively in response to conditions triggering pilot-column shutdown. Activation of these solenoids is part of a control circuit interfacing dechlorination to pilot-column operation, discussed in a later section.

Design and Operation of Pilot Scale Dechlorination System High-purity SO_2 was fed continuously from a 150-lb. gas cylinder equipped with a single-stage pressure regulator and purge valve (Matheson 13-660). A backup cylinder of high-purity nitrogen (N_2 grade 5; size 200 cylinder) was connected to the SO_2 regulator through the purge valve. Thus when the SO_2 cylinder was manually closed, N_2 could be fed through the SO_2 regulator into the flow system. When the SO_2 cylinder was changed, N_2 was used to purge residual SO_2 to a vent outside the treatment plant. In normal operation, effluent gas from the SO_2 regulator was injected into the pilot-column influent. Preliminary checks for leaks and tests of system performance were also performed using N_2 as the system gas.

From Figure 1, the principal SO_2 controls downstream of the regulator are seen to include: 1) a flowmeter (Brooks Model 1355 R-2-15 AAA) and needle valve (Model 8503 Valve with a Size 1 Non-Rising Stem); 2) a low-pressure switch (ASCO SB20A TE 20A32) to detect no SO_2, isolated by a Teflon membrane (Fluorocarbon GPC-142-S); 3) a solenoid (#3 - Fluorocarbon DV2-122 NC A2) to shutoff SO_2 flow in synchronization with conditions triggering pilot-column shutdown 4) a stainless steel manual shutoff valve 5) a check valve to prevent backflow of water.

As shown in Figure 1, SO_2 was injected downstream of a water pressure regulator and pressure gauge. The water pressure in the supply line was initially regulated to 20 psi. Prior to SO_2 injection, the water pressure was decreased to 10 psi (Table 1). Thus with 18 psi on the SO_2 pressure regulator, positive pressure could be achieved for SO_2 injection. These pressures were chosen with an understanding of system performance. Since SO_2 is liquified, the maximum pressure that can be obtained from the cylinder is 37 psi at 20 ^oC, which is more than adequate. Since the pilot scale dechlorination system was placed in the chlorination room, it was approximately 15 ft from the GAC pilot columns. Downstream of SO_2 injection, the water pressure decreased; by maintaining 10 psi at the point of dechlorination, there was still 4 psi at the head of pilot column 3. An influent pressure of 1.5 psi was sufficient to maintain flow through the GAC pilot column.

All components in contact with SO_2 gas were either stainless steel or Teflon. Teflon tubing was used in the SO_2 transfer line, and stainless steel tubing (1/8 in od x 24 in long) was used to inject SO_2 into the water stream. Initially, copper tubing (1/2 in id) was used to convey water through dechlorination. After about 10 weeks in service, a pinhole leak developed in the copper wall at the point of SO_2 injection, presumably due to a high local concentration of sulfuric and hydrochloric acids (cf. Table 2). This problem was eliminated by using a length of glass tubing (5/8 in od), connected with brass compression fittings and Teflon ferrules, at the point of SO_2 injection.

Control Circuit Interfacing Dechlorination and GAC Pilot-column Operation. Figure 3 shows a circuit that was built for centralized indication of conditions for operating the GAC pilot columns and dechlorination system. Depending on the combination of operating conditions in the system, six solenoid valves controlling flow of water and SO_2 could be either opened or closed. The solenoids are designated normally closed (NC) or normally open (NO) to indicate their position when no voltage is applied. This circuit was designed for convenience as well as safety, so that the experiment could be placed in standby with minimum effort when necessary.

As shown in figure 1, solenoid 1 (ASCO 8210 D95 NC) controlled the main water supply to the three pilot columns. A pressure reducer (Watts U5LP) in the main water supply line was used to reduce the influent pressure from approximately 70 psi to 20 psi. A dual pressure switch (ASCO SC10B TE10A32) placed in the main water-supply line controlled supply of electrical power to solenoid 1. This pressure switch would cut off the power supply to solenoid 1 if the water pressure exceeded 30 psi or fell below 5 psi. Above 30 psi, Teflon bead-to-bead couplings on the glass pilot columns (6 in id) would start to leak; below 5 psi, flow could not be maintained through 3 GAC beds but would go through the column bypass line. Either condition would close solenoid 1, while solenoid 2 (ASCO 8210 C13 NO) would open, diverting the water supply to the filters. To prevent the pilot columns from draining when solenoid 1 closed, solenoids 4,5 and 6 (ASCO 8210 C94 NC) on the pilot-column effluent lines would also close simultaneously. Likewise if solenoid 1 closed, solenoid 3 would close to shut off the flow of SO_2. Since solenoids 1, 3, 4, 5 and 6 are all designated NC, loss of power in the treatment plant could also effectively place the experiment in standby.

A pressure switch was also placed in the SO_2 line to detect a pressure too low for SO_2 injection, for example, less than 14 psi. The control circuit is wired so that loss of SO_2 closes solenoid 3 in the SO_2 line, as well as the pilot-column effluent solenoids 4,5 and 6. However, a toggle switch can override closure of solenoids 4, 5 and 6 when solenoid 3 is closed. This switch enables the pilot columns to be filled with water at the start of the experiment, when the SO_2 tank is manually shut off.

Chloroform Analyses: GAC and Water Samples Adsorption of chloroform was monitored in pilot columns 1 and 3, as a basis for evaluating their performance and the effect of dechlorination. Chloroform concentrations were determined in influent and effluent water samples, as well as in GAC samples collected from six sequential bed depths. Chloroform in water samples was solvent-extracted using hexane; chloroform in GAC samples was solvent-extracted using methanol and sonication. Hexane and methanol extracts were analyzed by gas chromatography with electron-capture detection; these methods of analysis are described in detail elsewhere (4).

RESULTS AND DISCUSSION

Performance of SO_2 Dechlorination System As indicated in Figure 4 and Table 1, SO_2 was injected at an average pressure of 18 ± 2 psi, with an average flow of 3.9 ± 1.6 ml/min. Therefore there was a 41% relative standard deviation in SO_2 flow.

Figure 5 shows the effect of SO_2 on influent water quality. The chlorine residual dropped from 1.24 ± 0.35 mg/L for pilot column 1, to 0.1 ± 0.1 mg/L for pilot column 3. Likewise, the pH dropped from an average of 7.2 ± 0.3 for pilot column 1, to an average of 5.3 ± 0.6 for pilot column 3. Calculations in Table 2 indicate that SO_2 was injected in a stoichiometric excess of 9:1. Although this is a relatively large excess, the dechlorination system described is based on the lowest range possible for manual control of gas flow. In Table 2, dechlorination is predicted to decrease the pH to 4.4. The actual decrease in pH to 5.3 was somewhat less. In fact, some SO_2 was consumed by reaction with MnO_2 to produce Mn^{2+}, which is water soluble. After 10-weeks' pilot-column operation, brown deposits of manganese dioxide were quite evident on the glass flowmeter tubes and glass walls of pilot columns 1 and 2, which received chlorinated influent. By contrast, there were no colored deposits on the surfaces of plumbing to pilot column 3, even after 30 weeks. Some of the excess acidity may also have been buffered by fulvic acids naturally present in the treated surface water.

Data in Figure 5 suggest that measurements of pH are at least as effective as measurements of chlorine residual for monitoring the operation of the dechlorination system. In fact, after 180 days, a drop in SO_2 pressure was observed at the regulator (cf Figure 4). Moisture was noticed in the flowmeter tube, and flow control did not seem reliable. Chlorine residuals above 0.1 mg/L were also detected in the influent to pilot column 3, indicating that the dechlorination system was malfunctioning. As shown in Figure 5, the pH increased dramatically from approximately 5.0 to 6.5. After shutting down the pilot-column system at 30 weeks, the dechlorination system was examined and made to work by installing a new SO_2 cylinder and regulator.

Performance of GAC Pilot Columns: Chloroform Adsorption Chloroform was found to reach breakthrough in the effluents of pilot columns 1 and 3 after 110 days, as indicated in Figure 6. This conclusion is confirmed by the data in Figures 7 and 8 for chloroform adsorption on sequential GAC bed depths: after 110 days, chloroform concentrations increased rapidly on GAC from 115 cm, essentially the bottom of both pilot columns. In Figure 8, the two pilot columns are also noted to have adsorbed similar total amounts of chloroform. Similar results were obtained for pilot columns at the Torresdale treatment plant, where a solution of sodium sulfite was used for dechlorination (5).

CONCLUSIONS

1. Continuous dechlorination was achieved for 180 days with a low flow of 3.9 ± 1.6 ml/min SO_2.
2. The pH decreased from 7.2 ± 0.3 to 5.3 ± 0.6 after dechlorination with SO_2.
3. Useful design features of the dechlorination system included: a) water pressure regulator b) SO_2 pressure regulator c) SO_2 flow control valve with a non-rising stem d) glass tubing at the point of SO_2 injection into water e) N_2 purge system f) circuit to interface dechlorination to pilot-column operation.
4. There was little difference in GAC adsorption of chloroform from chlorinated or dechlorinated filtered water.

ACKNOWLEDGMENT

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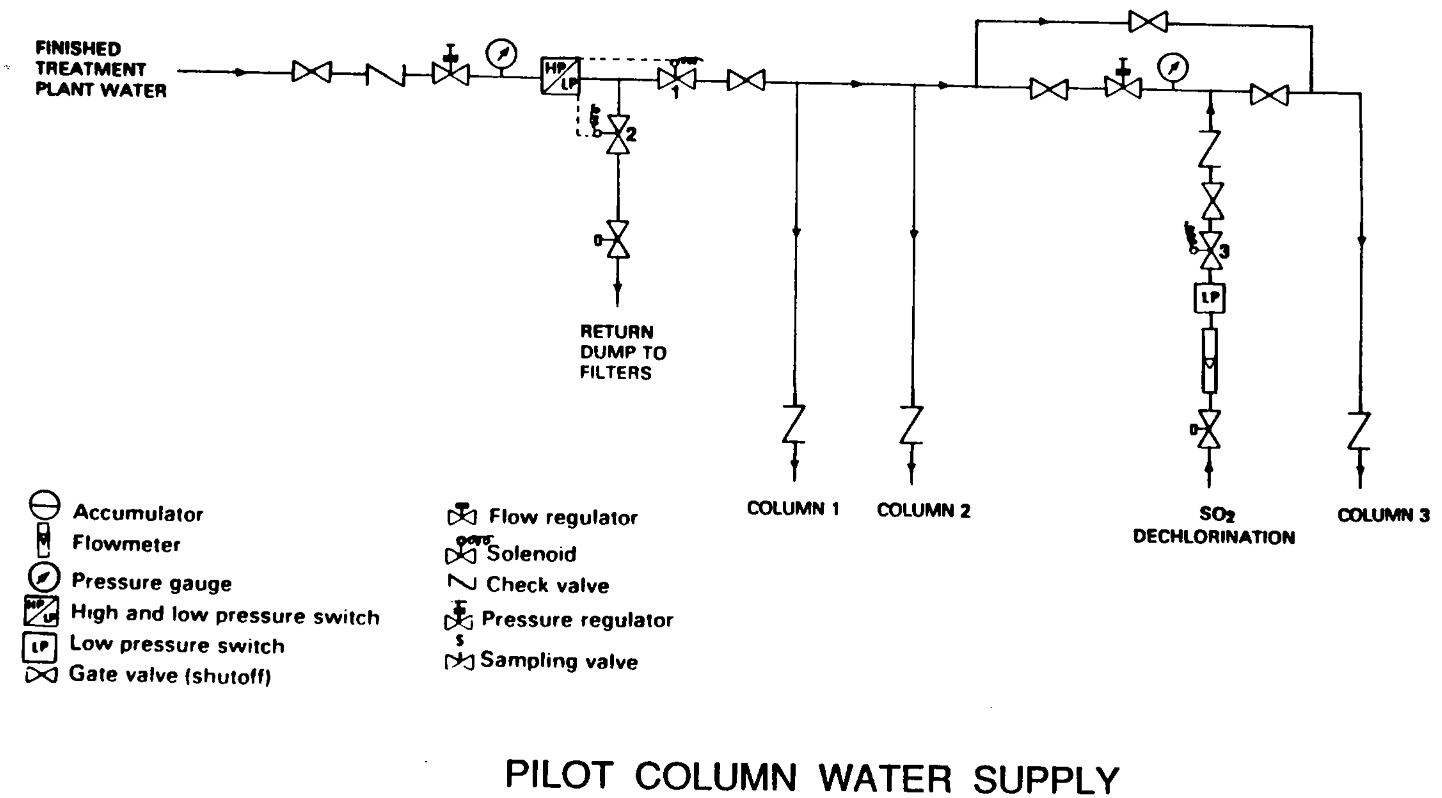

Figure 1 Schematic of Flow Path for Water Supply, Dechlorination, and GAC Pilot Columns.

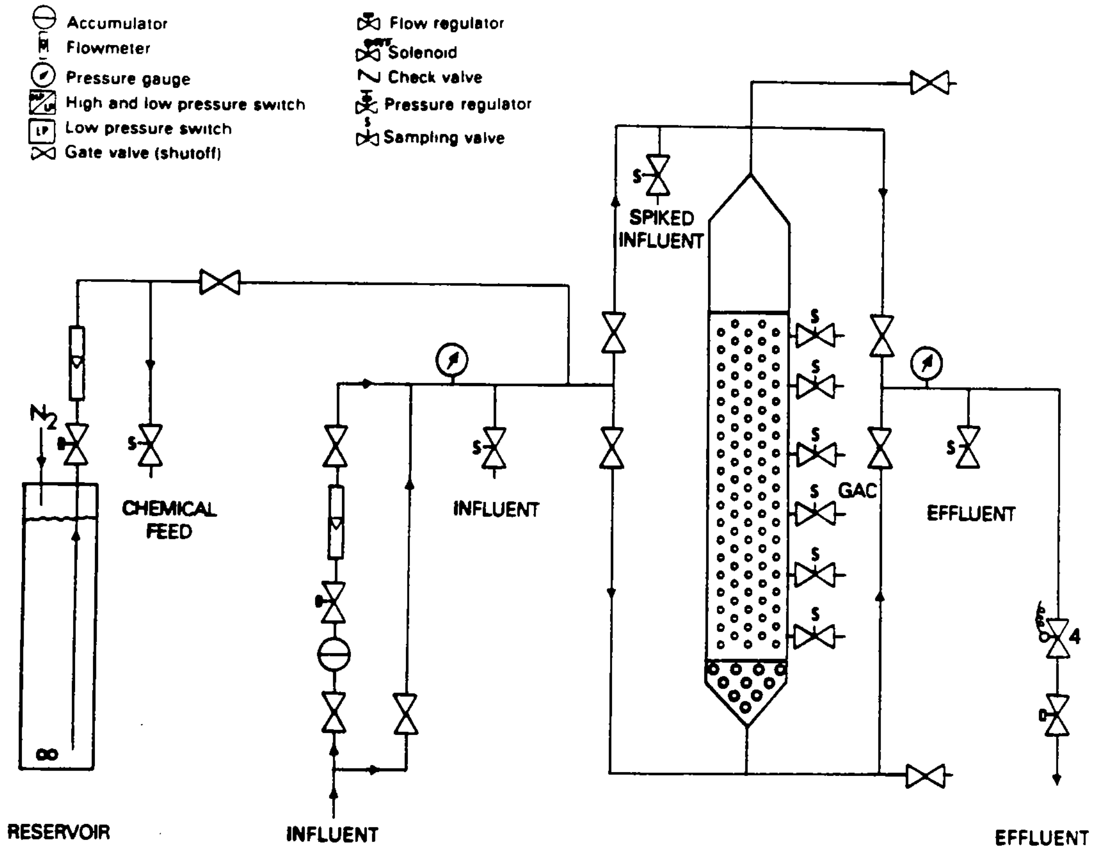

Figure 2 Schematic of GAC Pilot Columns and Ports for Sample Collection. Results in this paper are for pilot columns 1 (chlorinated influent) and 3 (dechlorinated influent), neither of which received inputs of synthetic chemicals from a reservoir.

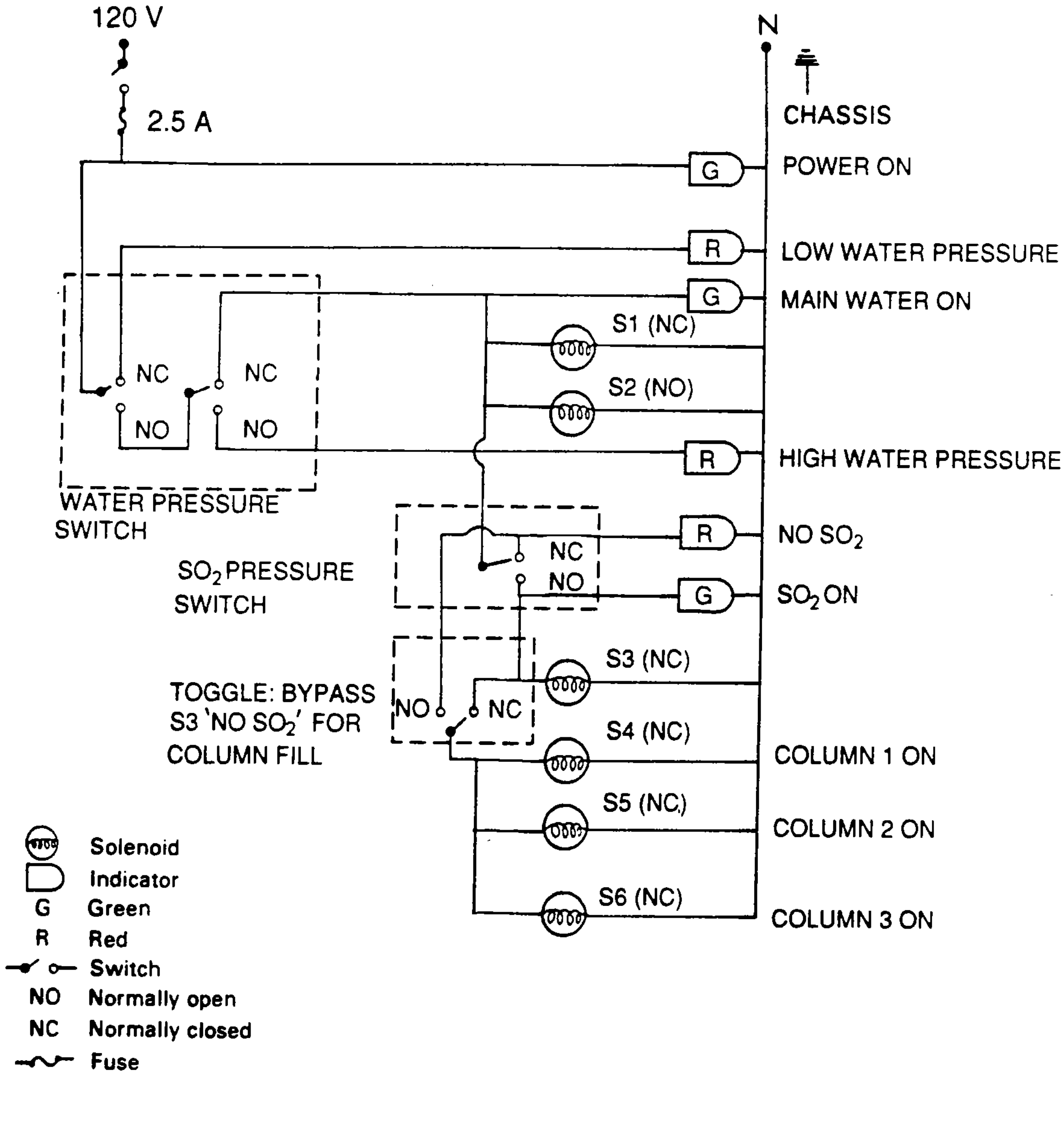

Figure 3 SO_2 Control Circuit to Interface Dechlorination to Pilot Column Operation. Location of solenoids 1 - 6 is indicated in Figure 1 (S1, S2, S3) and Figure 2 (S4, S5, S6).

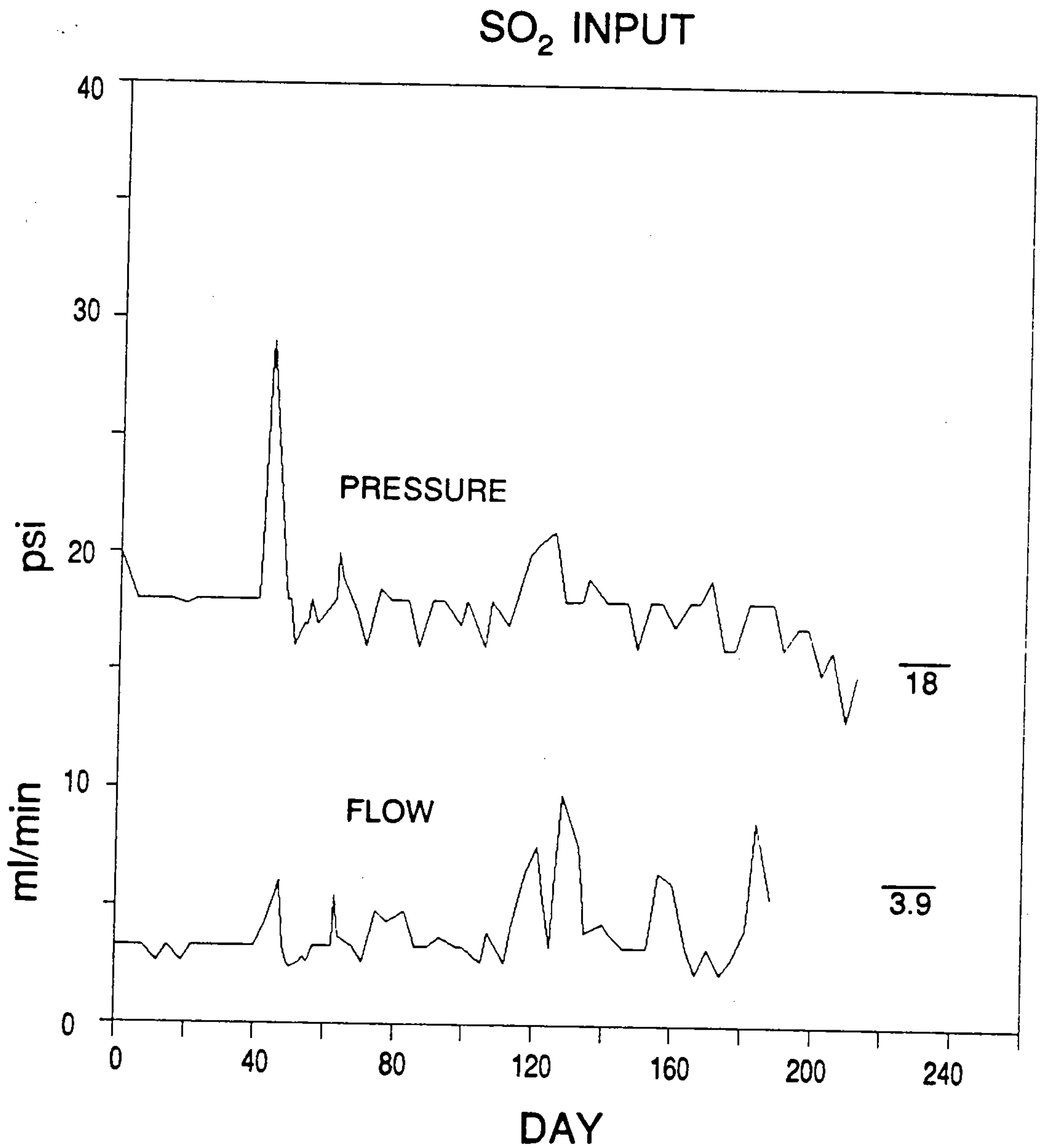

Figure 4 Flow and Pressure of SO_2 Injected into Influent of Pilot Column 3. After 180 days, the pressure of SO_2 in the feed line dropped; the flowmeter indicated a positive flow of SO_2, although moisture was evident in the tube. Results in figure 5 give a more definitive indication of a malfunction, which was later traced to the regulator on the SO_2 tank.

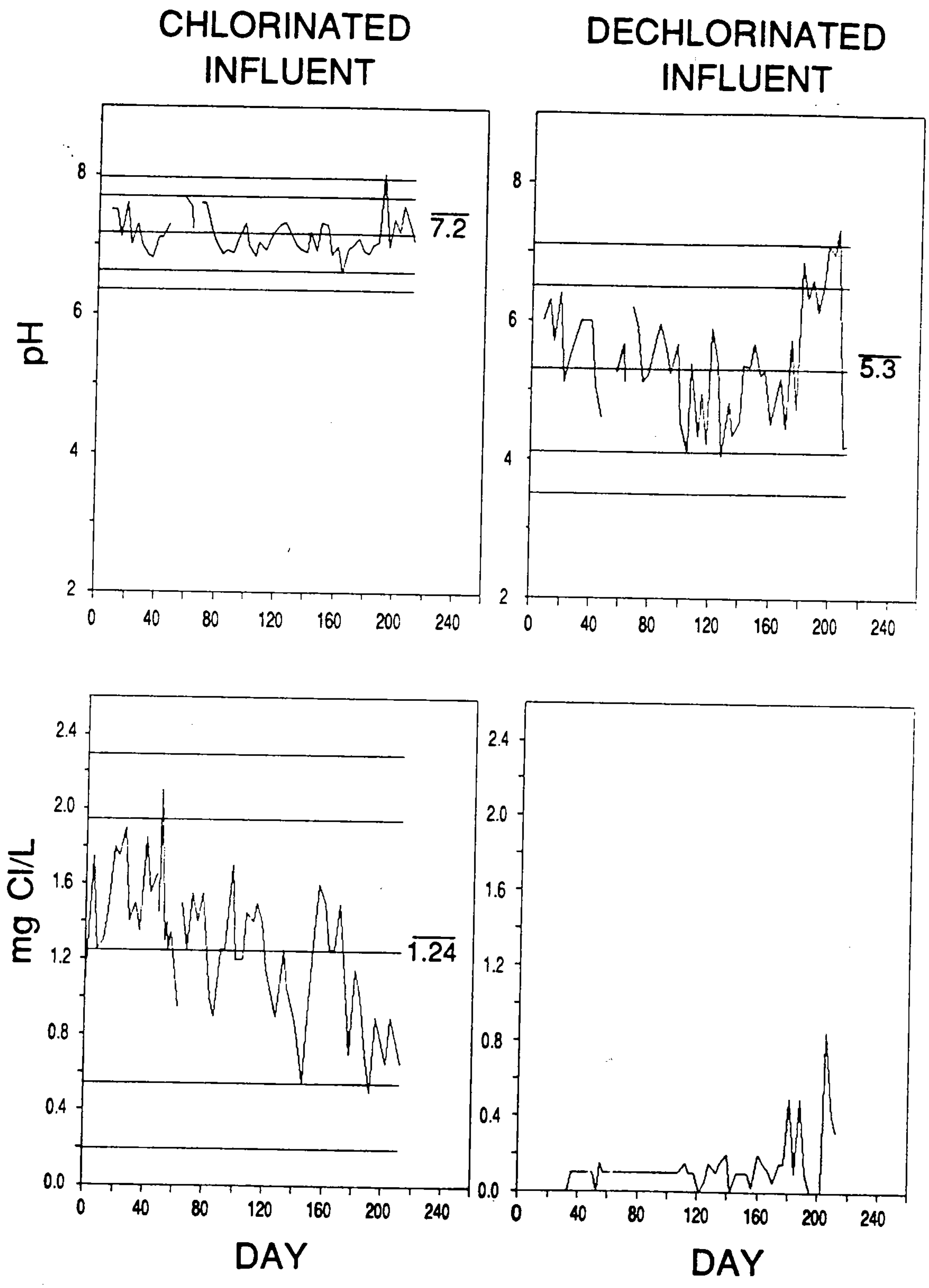

Figure 5 pH (Top) and Chlorine Residual (Bottom) in Influent to GAC Pilot Columns 1 (Left) and 3 (Right). After 180 days, the pH of the influent to pilot column 3 increased to near neutral, and a chlorine residual was detected. These results are considered to indicate a reduced input of SO_2. The regulator on the SO_2 tank was found later to be stuck.

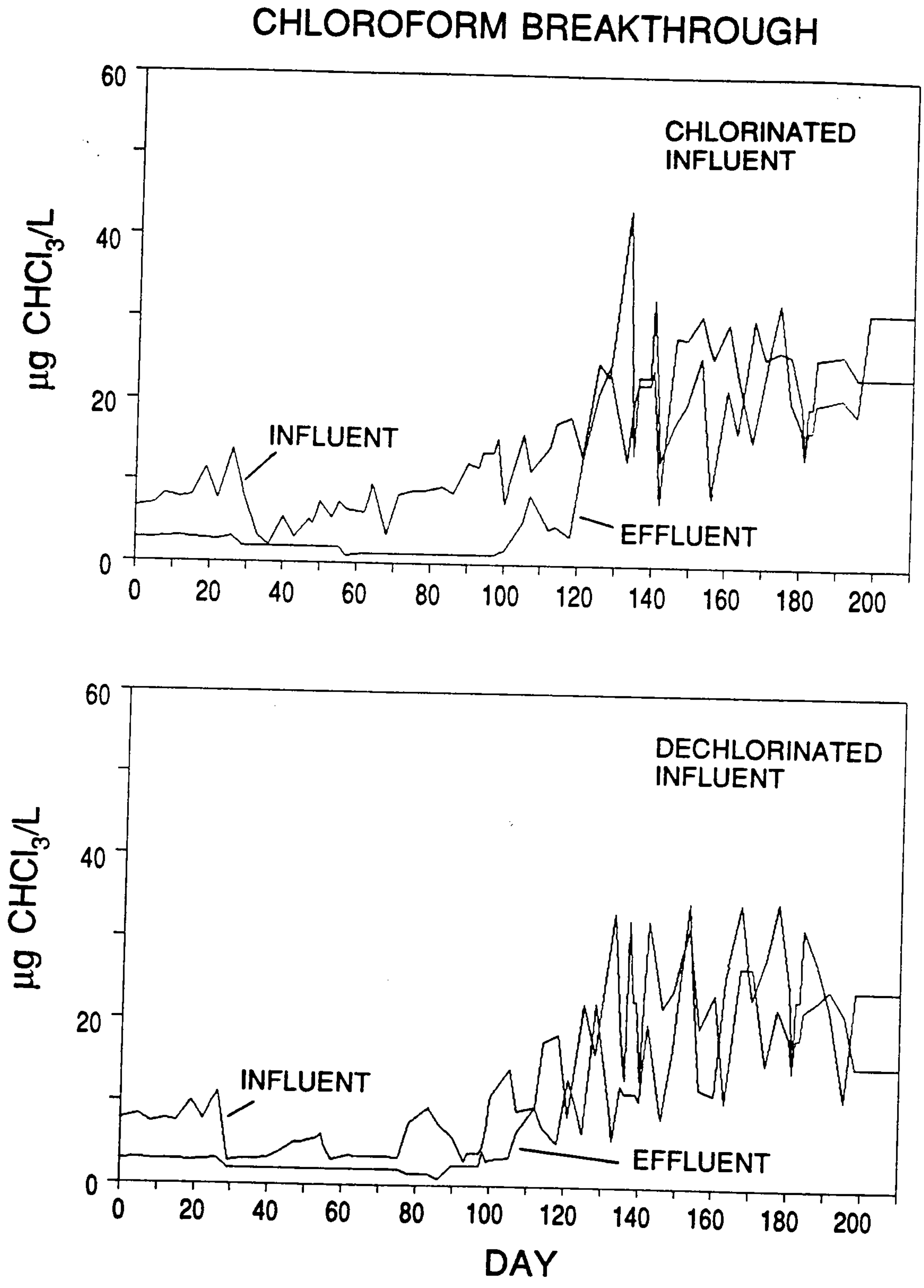

Figure 6 Chloroform Breakthrough Curves for GAC Pilot Columns 1 (Chlorinated Influent) and 3 (Dechlorinated Influent). Breakthrough was reached in both pilot columns after approximately 110 days in operation.

CHLOROFORM ADSORPTION-CHLORINATED INFLUENT

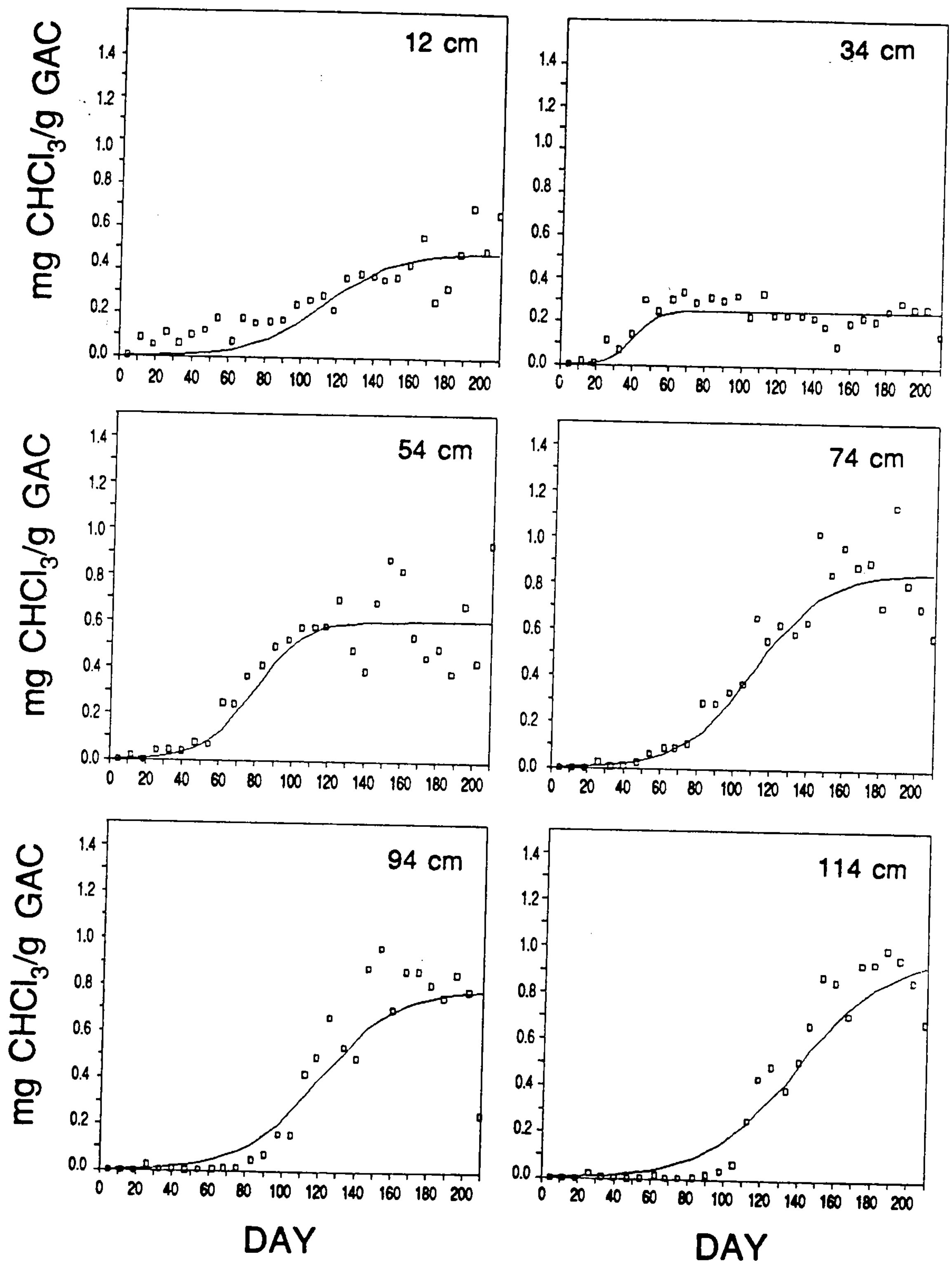

Figure 7 Chloroform Adsorption on Sequential Bed Depths of Pilot Column 1 - Chlorinated Influent

CHLOROFORM ADSORPTION-DECHLORINATED INFLUENT

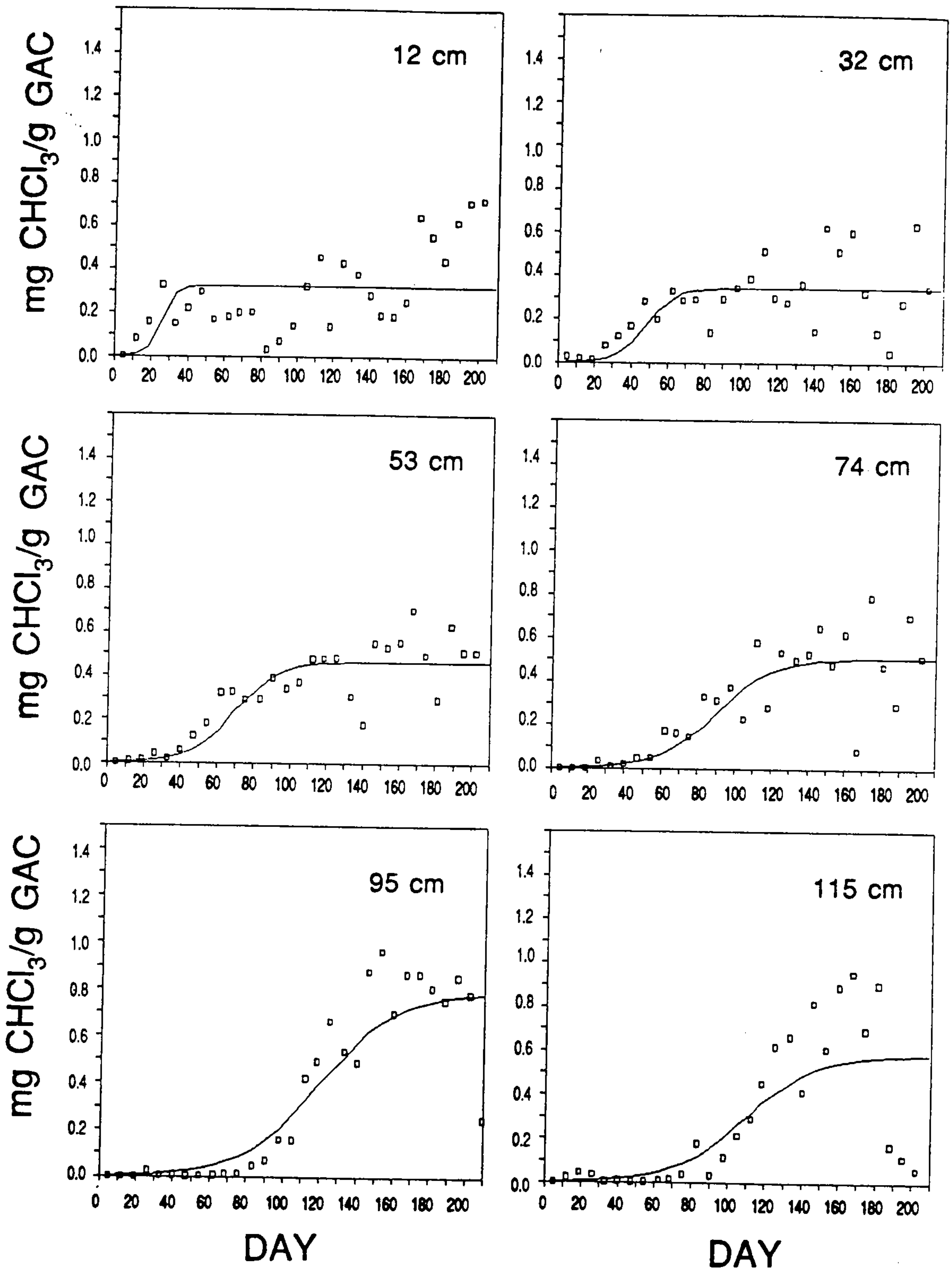

Figure 8 Chloroform Adsorption on Sequential Bed Depths of Pilot Column 3 - Dechlorinated Influent.

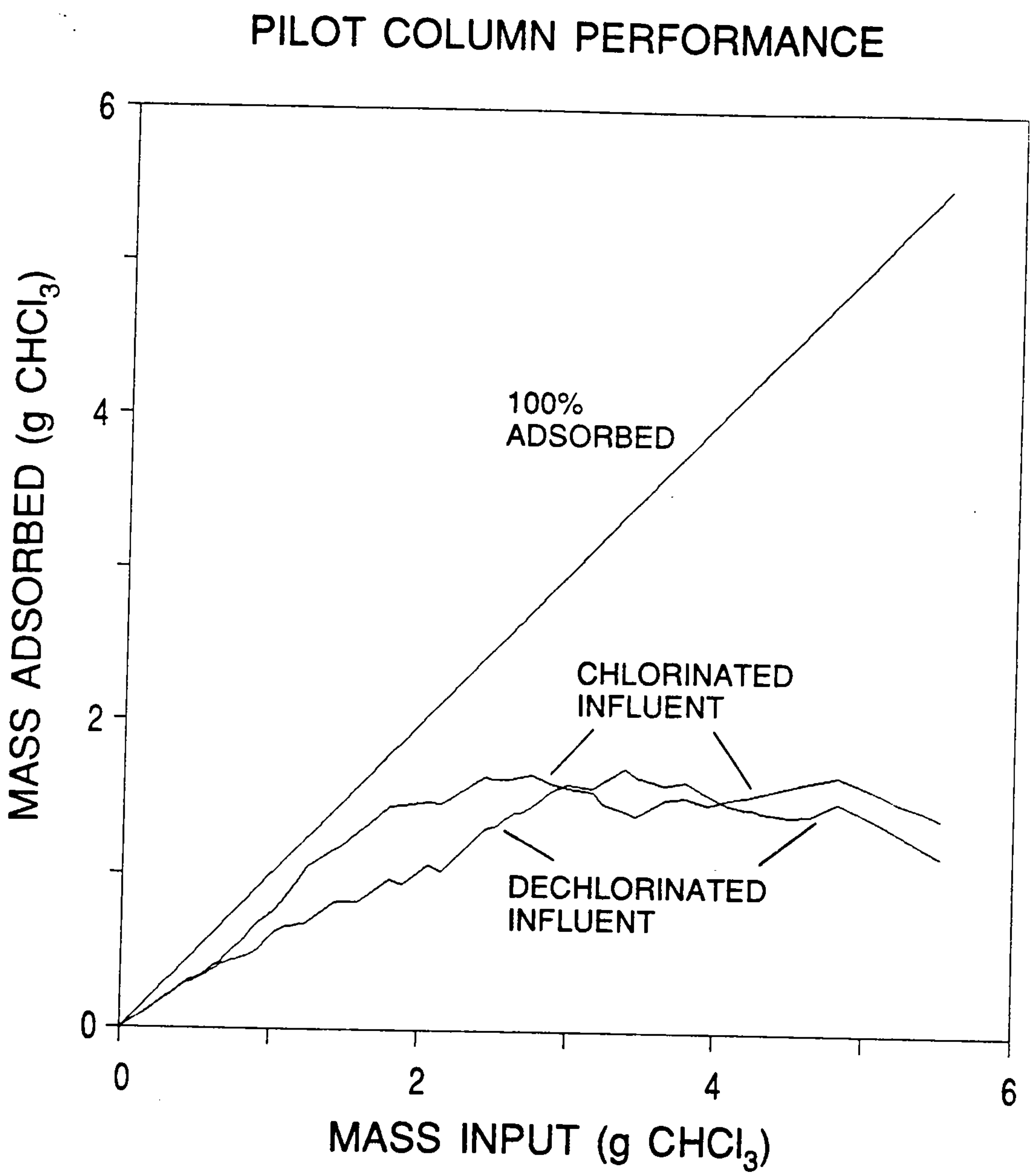

Figure 9 Pilot Column Performance: Cumulative Chloroform Adsorption on GAC Pilot Columns 1 (Chlorinated Influent) and 3 (Dechlorinated Influent).

Table 1 GAC Pilot-Column Operating Conditions: February 12, 1987 - September 11, 1987

		Pilot Column 1 Chlorinated Influent	Pilot Column 3 Dechlorinated Influent
Mass of GAC	kg	9.35	9.25
Calgon F400 12 x 40 mesh			
Bed Dimensions			
Diameter	cm	15	15
Cross Sectional Area	cm^2	182	182
Length	cm	116	118
Volume	L	21.1	21.5
Flow			
Mode		Downflow	Downflow
Flowmeter	L/min	1.43 ± 0.16	1.36 ± 0.22
Accumulator	L/min	1.24 ± 0.23	1.36 ± 0.23
Total throughput	L	379862	415791
Hydraulic loading	m^3/m^2-hr	4.21	4.62
Linear velocity	cm/min	6.82	7.46
Empty Bed Contact Time	min	17.0	15.8
GAC Bed Depths for Sampling (Equivalent Contact Times)	cm (min)	12 (1.8)	12 (1.6)
		34 (5.0)	32 (4.3)
		54 (7.9)	53 (7.1)
		74 (10.8)	74 (9.9)
		94 (13.8)	95 (12.7)
		114 (16.7)	115 (15.4)
Water Pressures			
Supply (range)	psi	15 - 20	15 - 20
Influent	psi	7.5 ± 2.5	4.0 ± 1.7
Effluent	psi	4.3 ± 2.5	4.1 ± 1.9
Dechlorination Conditions			
Water Pressure	psi	-	10. ± 0.6
SO_2 Pressure	psi	-	18. ± 2.
SO_2 Flow	ml/min	-	3.9 ± 1.6
Influent Water Quality			
Influent pH	-	7.2 ± 0.3	5.3 ± 0.6
Influent chlorine	mg/L	1.24 ± 0.35	0.1 ± 0.1
Water Temperatures			
Day 0: February 12	°C	3	3
Day 153: July 15 (max)	°C	30	30
Day 212: September 11	°C	22	22

Table 2 Calculated SO_2 Dose for Continuous Dechlorination

Reaction of Residual Free Chlorine and SO_2:

		$2\ H_2O$	+	SO_2	→	SO_4^{-2}	+	$4\ H^+$	+	$2e^-$
$2e^-$	+	$2\ H^+$	+	OCl^-	→	Cl^-	+	H_2O		
H_2O	+	OCl^-	+	SO_2	→	Cl^-	+	$2\ H^+$	+	SO_4^{-2}

Chlorine Residual in Influent: ~ 1.26 mg Cl/L
~ 0.92 mg OCl^-/L
~ 1.8×10^{-5} moles OCl^-/L

Flow Rate Through GAC Column: ~ 1.36 L/min
~ 1.37×10^4 L/wk

Chlorine Flow Rate: ~ 2.45×10^{-5} moles/min

Sulfur dioxide flow rate needed:

$$P \frac{dV}{dt} = \frac{dn}{dt} RT$$

$$\frac{dV}{dt} = \frac{dn}{dt} \frac{RT}{P}$$

P = SO_2 tank pressure 20 psi = 1.36 atm
R = 82 cc-atm/mole-deg K
T = 273 + 23 = 296 °K
$\frac{dn}{dt}$ = 2.45×10^{-5} moles/min
$\frac{dV}{dt}$ = 0.435 cc/min for 1:1 dose of moles SO_2 : moles HOCl

Flow of SO_2 at full scale - Brooks flow meter Model 1355CV R-2-15 AAA

Max flow SO_2 ≈ (Max flow air) $\sqrt{\frac{\text{specific gravity air}}{\text{specific gravity } SO_2}}$
≈ (49 cc air/min full scale) $(1.251/2.927)^{1/2}$
≈ 32 cc/min SO_2 full scale

Average Flow of SO_2 : ≈ 3.9 ± 1.6 cc/min SO_2

Stoichiometric excess of SO_2: ≈ $\frac{3.9 \text{ cc/min}}{0.435 \text{ cc/min}}$ ≈ 9.0

Effect of SO_2 Dechlorination on pH of Pilot-Column Influent

$[H^+]$ = 2 x (2.45×10^{-5} moles/min) / 1.36 L/min = 3.6×10^{-5} moles H^+/L = pH 4.4