



## Project Summary

# Treatment of Drinking Water by Bromide Addition and Powdered Activated Carbon Adsorption

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Although the phenomenon of the formation of trihalomethanes during the disinfection of drinking water with free chlorine has been known for over 10 years, water utilities are still seeking effective methods of control while maintaining good disinfection. This brief study was conducted to determine the feasibility of a new approach to trihalomethane control.

Reports in the literature state that predominantly bromine-substituted trihalomethanes are adsorbed on activated carbon better than are predominantly chlorine-substituted trihalomethanes. The goal of the proposed treatment scheme, therefore, was to minimize the concentration of trihalomethanes in finished water by adding bromide to water to deliberately create predominately bromine-substituted trihalomethanes that could subsequently be removed by powdered activated carbon.

The proposed treatment process did produce a water significantly lower in trihalomethane concentration than the formation potential in the source water. Two factors, however, worked against achieving the goals of the proposed treatment. One, when bromide is added to water, more trihalomethanes are formed, as expected. Two, apparently because of competition from other organics, these additional trihalomethanes, although bromine-substituted, did not adsorb on the powdered activated carbon used in these tests effectively enough to overcome the production of additional trihalomethanes. Furthermore, the residual bromide in the water after adsorption that stimulated the formation of trihalomethanes during post-chlorination resulted in higher trihalo-

methane concentrations in simulated tap water than would exist with conventional treatment. Therefore, unless natural waters would behave differently or another powdered activated carbon would be more effective in a competitive adsorption situation, this proposed treatment scheme cannot be recommended.

A second phase of this study was to determine the influence of pH, bromine concentration, and time on the formation of non-purgeable organic chlorine and non-purgeable organic bromine, as measured by neutron activation.

After 4 hours of exposure at constant bromide concentration, the concentrations of both parameters declined as the pH increased from 6.2 to 9.2. Possibly because of the slower oxidation of bromide at higher pH, however, this trend was not maintained when the pH reached 10.7.

At constant time and pH, the concentration of non-purgeable organic bromine increased as the bromine concentration increased, but the concentration of non-purgeable organic chlorine was not consistently correspondingly suppressed.

In the absence of bromide at constant pH, the concentration of non-purgeable organic chlorine increased as time increased from 4 hours to 6 days. In the presence of all three bromide concentrations studied (4.2, 8.4, and 16.8  $\mu\text{mol/L}$ ), however, the concentrations of both non-purgeable organic chlorine and bromine declined with time (from 4 hours to 6 days), sometimes to zero for non-purgeable organic bromine.

*This Project Summary was developed by EPA's Water Engineering Research*

**Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).**

## Background

The creation of chlorinated by-products during the disinfection of drinking water with free chlorine has been well documented. The details of this reaction and the various treatment options available to drinking water utilities to avoid high concentrations of trihalomethanes (THMs) in tap water have also been discussed in depth in the research literature.

In spite of this research — much of it successful — each of the techniques for THM control currently available to water utilities has disadvantages, either because of cost, degree of effectiveness, or interference with the disinfection process. The purpose of this project was to investigate the feasibility of a new treatment technique for THM control — a technique based on the principle of enhancing the formation of dibromochloromethane and bromoform during the THM formation reaction by adding a low concentration of bromide, thereby consuming most of the active precursor, and then lowering the THM concentration by adsorption on powdered activated carbon (PAC).

If most of the "active" (reactable) precursor could be consumed during the THM formation phase of the process, final disinfection with free chlorine should be possible without additional excessive THM formation. Further, if the dibromochloromethane and bromoform formed during the reaction phase of treatment could be economically adsorbed on PAC, the resulting tap water should meet the U.S. Environmental Protection Agency's (USEPA) Interim National Primary Drinking Water Regulation (INPDWR) for total trihalomethanes (TTHMs) of 0.10 mg/L. Even if effective, however, this process will only be considered successful if it does not aggravate the formation of other halogenated disinfection by-products measured as non-purgeable organic halogen (NPOX).

As an exploratory project, resources (funds and time) were limited. Therefore, after some preliminary experimentation to set boundary conditions, only one final test could be performed. Inconclusive, unexpected, or unsuccessful results could not be verified by repeat studies, under similar or revised conditions.

## Theoretical Considerations

Although removing all of the organic

carbon (TOC) from drinking water as a control strategy for preventing THM formation has intrinsic advantages, only a small percentage of the carbon in humic acid reacts with free chlorine to be incorporated into THMs, indicating that only a few sites on the precursor(s) are "active." Therefore, theoretically, if the "active" sites on the TOC in drinking water could be made to react and the reaction products could be removed, the remaining TOC should be unreactive. Driving the THM formation reaction toward completion and removing the reaction products should, therefore, prevent further formation of THMs in the distribution system during finished water chlorination.

Further, enhancement of the THM formation reaction will occur if the pH of the water is elevated. Conversely, other chlorination by-products, as measured by non-purgeable organic chlorine (NPOCl), do not form as readily at high pH.

In addition, because of the favorable adsorbability estimated for  $\text{CHBr}_2\text{Cl}$  and reported in the literature for  $\text{CHBr}_3$ , the THMs formed during free chlorination might be easily removed by adsorption on powdered activated carbon (PAC) if the predominant THM species were  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$ .

Finally, this will occur if a small amount of bromide is present or is added to the water before free chlorination. The presence of bromide increases the reaction rate of THM formation. Counter to these favorable features, however, is the feature that as the bromide concentration in water increases, so does the total quantity of TTHMs formed at higher pH, even though the TTHMs are mostly bromine-substituted. An unknown factor in the proposed treatment scheme is the influence of the presence of bromide on other disinfection byproducts, as measured by NPOCl and non-purgeable organic bromine (NPOBr).

## Objectives

Based on these theoretical considerations, this feasibility study was undertaken with the following objectives:

1. Assess the potential of the proposed treatment concept.
  - 1A. Determine practical reaction conditions of pH and bromide concentration that will:
    - a. minimize the  $\text{CHCl}_3$  concentration,
    - b. maximize the  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  concentration,
    - c. avoid excessive TTHM concentrations,
    - d. result in a high initial rate of THM formation, and
    - e. result in a high conversion of the total (6-day) precursor, as measured by THM formation potential (THMFP), to THMs in 4 hours.
  - 1B. Determine the adsorbability of the reaction products (THMs) on PAC in the presence of residual TOC and NPOX.
  - 1C. Determine the adsorbability of NPOCl and NPOBr on PAC in the presence of residual TOC and THMs.
  - 1D. Convert as much potentially reactive THM precursor to THMs as possible in the reaction phase, such that, after adsorption treatment, the water could be post-chlorinated without significant THM reformation.
2. Determine the influence of pH and bromide concentration on the formation of NPOCl and NPOBr.

## Experimental Procedures

### Formation of Trihalomethanes and Non-Purgeable Organic Halogen

The investigation of the influence of pH and bromide concentration on the formation of THMs was carried out in 500 mL amber bottles cleaned with a commercial acid cleaning solution and sealed head-space free with screw caps with Teflon® \* cap liners. The source of THM precursor was a commercially available soil humic acid (AHA), and the solvent was Houston tap water that had been passed through an adsorption bed of granular activated carbon (GAC) and a mixed bed ion exchanger. Free chlorine was provided by diluting commercial hypochlorite. Bromide was added as potassium bromide (KBr). Four bromide concentrations were studied; 0 mg/L, 0.5 mg/L KBr (4.2  $\mu\text{mol/L}$ ), 1.0 mg/L KBr (8.4  $\mu\text{mol/L}$ ), and 2.0 mg/L KBr (16.8  $\mu\text{mol/L}$ ). Before any experiment, a 6-day chlorine demand study was performed to ensure that in the actual experiment sufficient chlorine would be added to provide a free residual of > 2 mg/L at the end of the test.

In a typical THM formation test, four replicate bottles for each condition were filled with 5 mg/L of AHA in DI water, and the appropriate pH buffer, KBr, and free

\*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

chlorine dose were added. As a companion, four control replicate bottles were prepared. These controls were identical to the test samples except for the lack of any AHA. All samples were held at room temperature, about 25 °C. After exposure times of 4 hours (0.17 day), 1 day, 3 days, and 6 days, one test bottle and one control bottle was dechlorinated, in turn, with sodium sulfite. After the reducing agent was added, 65-mL, clean (solvent rinsed and baked at 150 °C for 1 hour) amber bottles were carefully filled and capped head-space free with screw caps with Teflon<sup>®</sup> faced septa. These bottles were stored at 4 °C until THM analysis. After the 65-mL bottles had been filled, separate 250-mL amber glass bottles were also filled head-space free for those cases where NPOX analyses were also to be performed. These bottles were stored at 4 °C until the particular experiment was over; then the bottles were shipped to the analytical laboratory by overnight courier.

### Analytic Procedures

To analyze for THMs, a liquid-liquid extraction (LLE) procedure was used with pentane as the extraction solvent. THMs were measured by gas chromatography with an electron capture detector.

### Procedures for Adsorption of Trihalomethanes and Non-Purgeable Organic Halogen

The test started with seven, square, 2-L jars being filled with 1.5 L of the GAC-treated DI water. To each of the jars was added 5 mg/L of AHA, 1 mg/L KBr (8.4 μmol/L Br), 500 mg/L NaNO<sub>3</sub> (to prevent the adsorption of interfering inorganic chloride and bromide), 10 mg/L free available chlorine (FAC), and 35 mg/L alkalinity as CaCO<sub>3</sub> (NaHCO<sub>3</sub>); the pH was adjusted to 6.9 with H<sub>2</sub>SO<sub>4</sub>. The seven jars (open) were then slowly mixed in a test apparatus for 4 hours.

After the reaction period was completed, 25 mg/L of Na<sub>2</sub>SO<sub>3</sub> was added as a dechlorinating agent to six of the jars and the jars were sampled for THM and NPOX analysis. The seventh jar continued to be slowly mixed for 2 more hours. This control jar was not given any further treatment, but was sampled for THMs and NPOX after 4 and 6 hours of reaction time to determine losses of THMs and NPOX, if any, to the atmosphere.

After dechlorination, each of the six jars received one of the following doses of PAC: 0, 5, 10, 25, 50, and 100 mg/L. After 30 minutes of contact with the adsorbent

with adequate mixing to prevent significant settling, 35 mg/L of NaHCO<sub>3</sub> (to ensure adequate alkalinity for good coagulation) and 100 mg/L of alum were added to each jar. All jars were then subjected to 1 minute rapid mix, 30 minutes of flocculation (slow mix), and 1 hour of settling.

The supernatant liquor was then decanted and filtered before being analyzed for THM and NPOX. After the supernatant liquor was removed, the sludge was placed in a graduated cylinder for further concentration. Finally, the concentrated sludge was membrane filtered before neutron activation analysis for NPOX. Water samples were analyzed for NPOX according to USEPA Method 450.1.

After removal of the sludge, the supernatant liquors were rechlorinated and stored in bottles for 3 days to simulate post-chlorination and passage through a distribution system. The samples were then dechlorinated and analyzed for THM and NPOX. Each of the six samples were compared with the 3.5 day, pH 7, 25 °C THMFP of the source water to determine the effect of the treatment scheme.

### Summary of Results

From the matrix of experimental conditions and based on the constraints chosen, the most practical reaction conditions for the formation of THMs were: pH, 7±; bromide concentration, 8.4 μmol/L (1 mg/L KBr); exposure time, 4 hours.

At the chosen conditions, after the 4-hour reaction period, the treated water had the following analysis:

Analyte	μmol/L	μg/L
CHCl <sub>3</sub>	0.28	33
CHBrCl <sub>2</sub>	0.28	46
CHBr <sub>2</sub> Cl	0.67	140
CHBr <sub>3</sub>	0.25	63
TTHM	1.48	282
NPOCl	3.29	117 as Cl
NPOBr	1.77	63 as Cl

Under the chosen reaction conditions, for a sample containing 5 mg/L of AHA as the THM precursor, 57 percent of the 6-day total THMFP, "total" precursor, was converted to TTHM, and the TTHM was 62 percent (CHBr<sub>2</sub>Cl + CHBr<sub>3</sub>) and only 19 percent CHCl<sub>3</sub>, on a μmol/L basis.

After a 4-hour reaction period, simple alum coagulation removed 16 percent of the TTHM, 45 percent of the NPOX, 35 percent of the NPOCl, and 60 percent of the NPOBr.

This same treatment resulted in 43 percent less TTHM in a simulated tap water

sample (3-day distribution time) than in untreated source water and 4 percent less NPOX, 2 percent less NPOCl, and 7 percent less NPOBr.

Treating the water with 50 mg/L of PAC for 30 minutes before alum treatment removed an *additional* 10 percent of the TTHM and an *additional* 25 percent of the NPOX, 28 percent of the NPOCl and 19 percent of the NPOBr when compared with simple alum coagulation removals. Increasing the PAC dose to 100 mg/L removed an *additional* 38 percent of TTHM and an *additional* 22 percent of NPOX, 36 percent of the NPOCl, and negative 6 percent of the NPOBr beyond alum treatment.

Treating the water with 50 mg/L of PAC before alum coagulation removed 68 percent of the 335 μg/L, 3.5-day THMFP in the source water and 60 percent of the 3.5-day NPOX formation potential (NPOXFP)—67 percent of the 3.5-day NPOClFP and 53 percent of the 3.5-day NPOBrFP. Increasing the PAC dose to 100 mg/L resulted in 77 percent removal of 3.5-day source water THMFP and 65 percent removal of 3.5-day source water NPOXFP—70 percent of the NPOClFP and 63 percent of the NPOBrFP.

The 50-mg/L-PAC-treated simulated tap water contained 0.11 mg/L TTHM and 0.06 mg/L NPOX as Cl and the 100-mg/L-PAC-treated simulated tap water contained 0.08 mg/L TTHM and 0.06 mg/L NPOX as Cl.

The proposed treatment approach was successful in lowering a high concentration TTHM formation potential in a simulated source water; it produced a simulated tap water that met the USEPA Regulation for TTHM without excessively increasing the concentration of other disinfection by-products, as measured by NPOX.

When compared with conventional treatment, however, the chosen PAC was unable, in competition with the other organic compounds present, to adsorb the additional THMs formed when bromide was added. Conventional treatment (no bromide added) produced waters containing TTHM concentrations of 33.8 μg/L and 28.5 μg/L for PAC doses of 50 and 100 mg/L, respectively, whereas the corresponding waters containing 1 mg/L KBr had TTHM concentrations of 60.5 μg/L and 58.3 μg/L. Three-day THMFP values were slightly higher in the samples containing bromide as well.

With the PAC used, adsorption of bromoform (as an example, THM) was 10 to 50 times less than adsorption in previous studies performed in "organic-

free" water. This was attributed to the competition from other organic compounds for adsorption sites.

In "organic-free" water, Nuchar® S-A was equal to or better than reports in the literature for the adsorption of chloroform, but was poorer for the adsorption of bromoform.

In contrast to the THMs, the organic compounds contributing to the remaining THMFP were well adsorbed on the PAC, being completely removed by the 25, 50, and 100 mg/L PAC dose.

NPOCl was poorly adsorbed by the PAC used and NPOBr was not adsorbed at all. The remaining NPOCl and NPOBr formation potential was hardly adsorbed at all in this study.

Only 0.24 µmol/L of 3-day THMFP remained in the water after rechlorination of the alum-coagulated and settled water. In contrast, 1.72 µmol/L of 3-day NPOXFP was found after this same water was post-chlorinated.

NPOCl and NPOBr could be analyzed in the sludges by neutron activation, but the mass balances indicated greater than 100 percent recovery of removed NPOCl and NPOBr.

In addition to the major objective of this study, an investigation was also conducted to determine the influence of the variables, pH, bromide concentration, and exposure time on the resulting concentrations of NPOCl and NPOBr, as determined by neutron activation. The following statements summarize the findings of this phase of the investigation:

NPOBr concentration declined more as pH increased than did NPOCl concentration, at a constant bromide concentration.

Although the NPOBr concentration increased as the bromide concentration increased, the NPOCl concentration was not consistently suppressed, as was the case with TTHMCl.

In the presence of all three bromide concentrations studied, as exposure time increased, the concentrations of NPOCl and NPOBr generally declined, sometimes to zero for NPOBr. In the absence of bromide, the concentration of NPOCl continued to increase from 4 hours' to 6 days' exposure, at all four pH values studied.

At a constant bromide concentration, after 4 hours' exposure, the distribution of chlorine to bromine is not influenced much by pH, either in the THMs or the NPOXs.

At a constant pH and 4 hours of exposure, the total quantity of halogen substituted into organic matter was about the same at bromide concentrations of 0, 4.2, and 8.4 µmol/L. When 2 mg/L of KBr (16.8 µmol/L) was added to the water, however, total halogen substitution rose.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-811659-01-0 by the University of Houston under the sponsorship of the U.S. Environmental Protection Agency.

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*Alan A. Stevens is the EPA Project Officer (see below).*

*The complete report, entitled "Treatment of Drinking Water by Bromide Addition and Powdered Activated Carbon Adsorption," (Order No. PB 86-171 410/AS; Cost: \$11.95, subject to change) will be available only from:*

*National Technical Information Service  
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# Project Summary

## Field Investigation and Evaluation of Land Treating Tannery Sludges

Robert M. Lollar and Waldo E. Kallenberger

Land treatment of wastewater sludges from tannery processes has been investigated during a five-year field plot study. The experimental design included eight field test plots receiving selected applications of three types of tannery sludges over a three-year period.

1. Two 0.2 hectare plots received beamhouse (hair-burn) sludge at two different sludge application rates (110 mt/ha and 220 mt/ha sludge). The 110 mt/ha sludge loading rate was selected to provide the assumed optimum loading of proteinaceous nitrogen.

2. Two total chromium loading rates (2240 kg/ha and 4480 kg/ha total chromium) were applied to two 0.2 hectare plots that received trivalent chromium-containing (chrome) sludge and to two 0.2 hectare plots that received mixed tannery (hair-burn and chrome) sludge.

3. A single 0.1 hectare plot received a triple total chromium loading (6720 kg/ha) of the mixed sludge, and a single 0.2 hectare control plot received no sludge addition.

The five-year study included analyses of sludge, soil core, plant-tissue, and soil pore and runoff water samples to evaluate the feasibility of land treatment of tannery sludges. The data generated indicated that land treatment is potentially an environmentally acceptable technology for management of wastewater sludges from trivalent chromium tanneries; however, waste application rates must be carefully controlled.

The applied trivalent chromium appeared to remain primarily in the top-

soil without any detectable oxidation to hexavalent chromium. Transport of trace quantities of chromium in soil runoff water appeared to be associated with movement of soil particles. Application levels of tannery sludges containing hair-burn wastes will be limited by the mineralization rate of the proteinaceous nitrogen and the crop inorganic nitrogen requirements. Elevated salt concentrations of the hair-burn sludges also will require specific consideration.

*This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The main objective of this project was to characterize the major technical and environmental aspects associated with the utilization of land treatment technology for the disposal of tannery wastewater sludges. Tanneries in the United States primarily utilize trivalent chromium coordination compounds in the conversion of skin and hide substance into leather. Total current annual generation of chromium-containing wastewater sludges is estimated to be approximately 25,000 metric tons (dry basis).

Tannery solid wastes containing chromium have for many years been applied to agricultural soils since they

contain proteinaceous, slow-release nitrogen. Wickliff, et al. (*Water, Air, Soil Pollution* 17:61-74, 1982) published the results of greenhouse investigations on the application of trivalent chromium-containing tannery wastewater sludges to two soils. Crops utilized were tall fescue, hybrid sweet corn and bush beans. These workers concluded that tannery sludge may be applied to soils as a fertilizer amendment without adversely affecting soil chemical properties. Furthermore, the amount and frequency of sludge application should be determined by: total and available nitrogen; total salt content; total and available chromium; and soil organic matter.

However, there has not been a definitive field study which would provide data on the design, operation and closure of tannery land treatment sites. A five-year field site investigation utilizing tannery wastewater sludges was designed to provide the necessary data. The project had three specific objectives:

1. To assess potential adverse impacts of land treatment on various environmental sectors.
2. To estimate the accumulation, degradation and migration of soil contaminants.
3. To provide data for the optimization of site design, operation and closure.

## Procedure

A suitable field site was located within the Scott Creek Valley in western Santa Cruz County, California. The actual study site was located on a small, almost level marine terrace remnant lying about 115 m above the floor of the valley. The soils of the marine terraces are about 1.5 m deep with a thick, well developed B horizon; they have low permeability.

Test plots, 0.2 hectare in area, were constructed at the site with fencing, wells, berms, roadways and drainage systems. PVC pipes connected the collection boxes at the base of each test plot to concrete sedimentation vessels equipped with V-notch weirs for discharge measurement.

Two types of tannery sludges were applied to the field site test plots at four different time intervals from June 1981 until October 1983. The proper amount of each sludge was spread on the appropriate experimental plot and incor-

porated into the topsoil to a depth of approximately 15 cm by tilling.

Analyses of sludge, soil core, grass, and soil pore and runoff water samples from each plot were conducted throughout the project period. Parameters receiving special attention were: chromium, total Kjeldahl nitrogen, salt, and nitrate-nitrogen.

## Results

Although the project data indicated that the applied trivalent chromium remained predominantly in the plot topsoil, there was some apparent movement of trace level amounts of chromium in runoff water which appeared to be associated with movement of soil particles. Hexavalent chromium was never detected in any of the sludge, soil core, or soil pore and runoff water samples. Data from Ribgut grass tissue analyses indicated no increase in chromium at the 2240 kg/ha sludge loading level. At the mixed sludge triple loading (6720 kg/ha) level, enhancement in plant tissue chromium was suggested by the data; however, the results were considered inconclusive due to the limited number of samples analyzed.

Trivalent chromium concentrations found in the soil below the plow zone before the first and following the last sludge applications were:

Soil Depth	Chromium - mg/kg	
	Background	May 1984
30 - 60 cm	29 - 49	11 - 73
60 - 90 cm	24 - 49	33 - 102

However, the chromium material balance in the top 15 centimeters of soil was not complete; as shown by the following:

Plot Loading	Chromium - mg/kg		
	Estimated Loading	Found	
		Average	Range
Cr Sludge - 1	1100	640	590-700
Mixed Sludge - 1	1284	1390	1240-1540
Cr Sludge - 2	2130	1620	1380-1800
Mixed Sludge - 2	2310	1190	1080-1300
Triple Loading	3530	2320	2010-2500

Sampling and analytical variability for both sludges and soils contribute to this incomplete recovery. The data obtained during the five-year study indicate a significant increase in the chromium level in the topsoil of the five treated plots.

Mineralization rates for the proteinaceous nitrogen in tannery sludges currently are not available in the literature and were not determined during this study. Soil water samples in March 1985 from the triple loaded plot had a median nitrate-nitrogen value of 42 mg/l. It is assumed that leaching problems associated with land application of tannery sludges would be eliminated if sludge application rates were limited to the optimum loading level which would provide for the nitrate-nitrogen demands of the plant growth. Furthermore, the project data indicated that the salt content of the hair-burn beamhouse sludges should be considered in loading decisions.

## Conclusions

Land treatment provides a potentially environmentally acceptable technology for management of tannery wastewater sludges from trivalent chromium tannery processes if sludge application rates are carefully controlled. The utilization of land treatment technology for management of these sludges must include the following considerations:

1. Chromium tannery wastewater sludges are characterized by a significant organic Kjeldahl nitrogen content (2 to 4.5 percent) which primarily results from the proteinaceous materials in the animal hides which are converted into leather in the tannery. Therefore, land treatment of these sludges should be guided by the mineralization rates of the proteinaceous nitrogen and by the inorganic nitrogen demands of the plants grown on the treatment site.

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2. Chromium tannery wastewater sludges are characterized by significant salt contents (4 percent sodium on a dry basis from unhairing wastewater sludges and 2.7 percent from the chromium-containing wastewater sludges). Land application of these sludges may result in poor grass germination and weed intrusion; therefore, careful attention should be paid to these possible salt effects, especially when the unhairing wastewater sludges are to be applied.

3. Trivalent chromium in tannery wastewater sludges remains primarily in the topsoil after land treatment, however, there may be some limited transport of chromium in soil pore and runoff water. The transport in runoff water is assumed to be associated with soil particle movement.

4. Hexavalent chromium was not detected during this five-year field study; therefore, it is assumed that applied trivalent chromium will not oxidize to the hexavalent form in this soil environment.

## Recommendations

This five-year field plot study was the first in-depth field investigation of the land treatment of chromium tannery wastewater sludges. The study results disclosed certain areas in which the project efforts could have been improved by additional prior information. The following recommendations are made for further study which would facilitate future utilization of land treatment technology for management of tannery wastewater sludges:

1. Improved sludge and soil sampling protocols which recognize the high analytical heterogeneity of the substrates should be developed.

2. Inter-laboratory analyses of sludge and soil samples by EPA Method 3050, SW846, Test Methods for Evaluating Solid Wastes, 1982, showed satisfactory agreement for total chromium and calcium. Future work involving tannery waste should restrict sludge and soil analysis to EPA Method 3050, SW846.

3. Improved agricultural practices to attain more uniform sludge incorporation into the topsoil and to secure grass or other crop growth are needed. The effect of the high sodium content of the air-burn sludge on the weed intrusion into the test plots also requires further consideration.

4. Proteinaceous nitrogen mineralization rates for wastewater sludges

from chromium leather tanneries were not found in the literature. Combined laboratory and field studies directed toward these mineralization rate determinations are recommended.

5. Chromium transfer from the topsoil appeared to be limited; the chromium which was transported in soil water runoff appeared to be associated primarily with movement of soil particles. Further field studies are recommended to determine the ultimate form in the topsoil of the added chromium. Dehydration of trivalent chromic hydroxide forms very insoluble trivalent chromic oxide. Soil physical chemical studies to provide data on the physical form of the chromium in the topsoil would be desirable to establish the upper permissible limit for trivalent chromium addition to topsoils.

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**Don A. Clark** is the EPA Project Officer (see below).

*The complete report, entitled "Field Investigation and Evaluation of Land Treating Tannery Sludges," (Order No. PB 86-176 542/AS; Cost: \$16.95, subject to change) will be available only from:*

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