



NJ Department of Environmental Protection and Energy  
Division of Science and Research  
CN 409, Trenton, NJ 08625-0409

## RESEARCH PROJECT SUMMARY

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### **Evaluation of Chemical and Physical Characteristics of Water Treatment Residuals Before and After a Freeze-Thaw Cycle**

Research Project Summary Prepared By:

Eileen A. Murphy  
**NJDEPE Project Manager**

Brian Dempsey  
The Pennsylvania State University

Mark Lunetta and Steven Elias  
The Pennsylvania State University

James DeWolfe  
Gannett Fleming, Inc.

#### **Principal Investigator(s)**

#### **ABSTRACT**

*The effects of natural freeze/thawing on the chemical and physical characteristics of eight NJ water treatment residuals were investigated in relation to trace metal leaching. Field and laboratory studies indicate that leaching of metals from residuals which have undergone a freeze/thaw cycle is considerably less than raw residuals. Furthermore, freeze-thawed residuals mixed with NJ soils leached metals less than raw residuals mixed with soils. The freeze/thaw residuals-soil mixtures, in most cases, exhibited leaching characteristics similar to those of the soils alone.*

#### **INTRODUCTION**

Water treatment residuals (WTRs) are by-products of water purification systems in which undesirable attributes of the raw water such as turbidity, color and dissolved solids are removed by a variety of physical and chemical processes. WTRs have commonly either been returned to the source waterway downstream of the treatment plant intake or have been released to a municipal sanitary sewer. Both of these methods of disposal of WTRs have become unattractive for a variety of reasons.

As the alternatives to disposal of WTRs have decreased in recent years, more attention has focused on beneficial reuse of the material. One such

beneficial reuse is land application.

Application of WTRs to soil has been the focus of numerous studies in recent years (Bugbee & Frink, 1985; Elliott *et al.*, 1990; Grabarek & Krug, 1987; Novak & Sievers, 1977). As the ultimate fate of potential environmental pollutants receives more attention from the regulating community, it is necessary to develop a firm understanding of the interrelationships, both beneficial and adverse, which develop when a waste such as WTR is applied to the soil. Most of the laboratory and field-scale studies for land disposal have focused on soil physical properties and on plant growth, especially the influence of aluminum residuals on the availability of phosphate to plants. This study focuses on the trace metals leaching potential of WTRs and WTR-soil mixtures. Specifically, this study investigated metals leaching from WTRs which have undergone a freeze/thaw cycle, since this method has been shown to be effective as a means of dewatering WTRs (Martel & Diener, 1991; Tsang & Vesilind, 1990)

#### **OBJECTIVES**

The primary objective of the work presented was to examine the effects of freeze-thaw (F/T)

dewatering on the physical and chemical characteristics of WTRs. This was accomplished by examining the physical process of F/T dewatering both in the field and in the laboratory and by examining the leachates and the chemical extracts that can be produced from the raw or wet WTRs and from the F/T WTRs. In addition, the chemical and physical behavior of soil-WTR mixtures was examined so as to determine the potential for release or mobilization of trace metals from the soils, the WTRs and from soil-WTR mixtures.

## PROJECT DESIGN & METHODS

Eight WTRs were used in this study, five from water treatment facilities in NJ and three from PA. Efforts were made to collect WTRs from facilities representing a variety of conventional treatment processes, especially with varying ratios of coagulant to contaminant concentrations. The WTRs were examined for various physical and chemical characteristics. The characteristics of the selected WTRs as well as detailed experimental techniques used are described in the full report. Field and laboratory experiments were performed concurrently.

Field F/T experiments were conducted using nine 4' by 8' test cells located at Jumping Brook Treatment Facility of the NJ American Water Co.. Three application techniques (one 3 inch application; two sequential 3 inch applications; and one 6 inch application) were evaluated for three NJ WTRs (Table 1). The effects of freezing on the solids content and the chemical and physical characteristics of WTRs, F/T WTRs and freezates were determined.

All eight WTRs were evaluated in the laboratory experiments, which included evaluations of the F/T mechanism, measurement of the physical characteristics of the F/T dewatered WTRs, and measurement of the chemical characteristics of WTRs and soil-WTR mixtures. The first objectives of the laboratory F/T experiments were to determine the rates and effects of the F/T process, especially regarding the solids content of the drained residues. In addition, the extent of recombination of water with F/T WTRs and WTRs that had been dewatered by centrifugation or air-drying processes was investigated.

Five WTRs in both the wet and F/T dewatered forms were selected for further evaluation of chemical properties. The WTRs were characterized by pH,

total organic carbon (TOC), total phosphorus, total Kjeldahl nitrogen (TKN), and total metal concentrations (aluminum, cadmium, copper and zinc). In addition, various extractions were performed (e.g., dithionite-citrate-bicarbonate aluminum and sequential fractionation of metals) to permit deduction of the speciation and availability of metals from WTRs with special focus on Al, Cu, and Zn. Actual analyses were performed using flame atomic absorption spectrometry.

Finally, the mobility of trace metals due to leaching from soil-WTR mixtures was evaluated. Five WTRs (each in both wet and F/T forms) were combined with two NJ soils (Adelphia and Flemington soils). These mixtures were examined by a variety of soil tests: pH, TOC, plant extractable phosphorus, TKN, cation exchange capacity (CEC), total trace metals, DCB extractable Al, sequential fractionation of trace metals, and a diagnostic (Baker) soil test for the availability and activity of various metals. Results were compared with respect to the form of the WTR (wet or F/T) and, where appropriate, to results for the soils or the WTRs alone. In addition, these soil-WTR mixtures were packed into columns and eluted with a calcium nitrate / sodium nitrate solution. Effluent pH, TOC concentration and metals concentrations were measured as a function of time and cumulative leachate flow. A more detailed explanation of each of the techniques used is available in the full final report.

## RESULTS

### *FIELD STUDIES*

The field tests have demonstrated the ease with which WTRs can be frozen under NJ conditions. In every case, applications were performed when the air temperature was less than  $-4^{\circ}\text{C}$  and when temperatures were forecast to be below freezing for at least three days following the application. The time to freeze ranged from 2 days for the 3 inch applications to 15 days for the 6 inch applications.

In the field tests, the total solids (TS) of the WTRs increased from 1-5% (initially) to 22-40% at two weeks after application to 75% within four weeks after application.

Table 1 shows metals concentrations in wet and F/T residuals before and after F/T cycles. Residual A is generated from a NJ plant using an alum flocculate plus a cationic polymer. Copper sulfate is used for algal control in the reservoir. Residual B is generated from a NJ plant which uses

an alum flocculating agent, and Residual C, from a NJ plant which uses poly-aluminum chloride and a cationic polymer. Metals analyses performed on the supernatants and freezates revealed that manganese concentrations were relatively high in most samples. This indicates a reducing environment both during storage of the WTRs and also in the freeze beds. This characteristic was true for all WTRs and for all times that were tested. For iron, total and filtered concentrations were lower than for manganese and the filtered concentrations only approached total leachate concentrations after more than one day of storage in the freezing beds. With the exception of manganese and zinc, most metals with detectable concentrations increased at one week and then decreased to near the original levels at three weeks. This indicates that metals present in the WTRs are released during the freezing process and are subsequently tied up thereby becoming unavailable for leaching once dewatering is complete.

#### *LABORATORY FREEZE/THAW AND REABSORPTION OF WATER*

The behavior of WTRs during laboratory freeze-thaw duplicated the field behavior in terms of the percent TS obtained immediately after F/T and after air-drying. F/T WTRs had a "coffee ground" appearance and were easily dewatered by gravity drainage, resulting in residuals with approximately 25% TS. Air-dried, F/T residuals dried out to greater than 70% TS very rapidly. F/T dewatered WTRs required only two days of drying at +25°C to exceed 70% TS, while raw residuals required more than six days.

Several variables were investigated. A colder lab freezing temperature (-13°C rather than -5°C) caused small changes in percent TS. Keeping WTRs 100% frozen for longer periods of time (two weeks instead of two days) caused slightly more effective dewatering. Two F/T cycles instead of one resulted in slightly more effective dewatering. Freezing thicker layers of residual, five inch depths instead of three, caused slightly more effective dewatering. Partially freezing a WTR resulted in ineffective dewatering. The benefits of F/T dewatering is not obtained from partial freezing.

F/T dewatered WTRs did not resorb water even with constant agitation. Air-dried and centrifuge dewatered WTRs did resorb water. With agitation, these physically dewatered WTRs resorbed all of the water provided.

#### *MOBILIZATION OF TRACE METALS - LEACHING COLUMNS*

Copper was released in greater amounts from columns packed with soil-WTR mixtures prepared with the wet WTRs than from columns packed with mixtures prepared with the corresponding F/T dewatered WTRs. An example of mass of copper eluted from one WTR is shown in Figure 1. Results of the diagnostic (Baker) soil test support the observations of the column experiments that a greater mass of copper was eluted from soil-WTR(wet) mixtures than soil-WTR(F/T) mixtures. Zinc displayed elution behavior essentially different from that of copper (see Figure 2). Results suggest that while more zinc may be released initially from the soil-WTR(wet) combination, as elution progresses, a greater mass of zinc may be released by the soil-WTR(F/T) combination. In fact, the mass of zinc released by the columns containing soil alone may actually surpass the mass eluted from the columns containing soil-WTR(wet) combinations. Cadmium was not released to a measurable extent from soil-WTR mixtures. Aluminum was not released by any of the soils or soil-WTR combinations at detectable concentrations.

The total mass of a metal contained in a WTR or a WTR-soil mixture was not a uniform indicator of the leachability of that metal. While a high copper concentration in combinations prepared with one wet WTR was indicative of higher copper concentrations eluting from those columns, the high zinc concentration of another wet WTR was not indicative of a similar release of zinc from the combination prepared with that WTR.

#### *SOIL FERTILITY AND PLANT NUTRITION*

The F/T dewatering process significantly decreased the concentration of TKN in the F/T dewatered residual as compared to the wet residual. The percentage decrease ranged from 7.5% to 11.7% for six WTRs resulting from the precipitation of aluminum. A similar decrease was not observed for total phosphorus indicating that phosphorus in a wet WTR partitions with the solid phase during F/T dewatering.

The addition of WTRs to soil decreased the concentration of plant available phosphorus in the soil. The form of the applied residual, however, may have a great impact on the magnitude of the decrease. It was observed here that wet WTRs, when combined with soil, decreased the level of plant available phosphorus to a greater extent than do WTRs applied

after having undergone F/T dewatering. These results suggest that an investigation into the availability of phosphorus as a function of WTR form (wet or dry) and of the extent of mixing may yield results which will aid in the understanding of how incorporation of WTR with surface soils affects plant growth.

## CONCLUSIONS AND APPLICATIONS TO NJ

### FIELD STUDY

The initial thickness of the residual application in the test cells influenced the time it took for complete freeze and the degree of freeze. Three inch applications worked best and are recommended for practical situations, although 6 inch applications (or sequential 3 inch applications over time) also eventually froze. However, the time required for complete freeze with the 6 inch applications make it an impractical alternative.

Metals were associated with the solid phase rather than in supernatant implying that, except for the first drain, thaw water is low in metals concentrations within three weeks after the freeze.

Natural F/T treatment of WTRs seems to be a very effective dewatering method for NJ residuals. NJ winter conditions are compatible with the successful application of the F/T process. For complete freezing of 3 inch applications of residuals, 3 days of subfreezing temperatures were required. The winter of '92 was mild but was adequate for complete freezing of these materials. Possibly, thicker applications can be used during more severe winters. More research is needed, however, to determine the effect of daytime thaw/nighttime freezing on residuals where F/T is being used for dewatering.

### LABORATORY FREEZE/THAW AND REABSORPTION OF WATER

Residuals which have undergone F/T resorb very little water. F/T dewatered WTRs are therefore very good candidates for alternate beneficial reuse plans in NJ. Resorption of water would result in considerable loss of strength as well as swelling. F/T residuals maintain their physical integrity even in the presence of water.

Very cold temperatures and long, sustained cold periods are useful for accelerating the freezing process. However, the quality of F/T WTRs is not substantially improved due to freezing at more severe conditions. NJ conditions are conducive to effective dewatering using natural F/T.

## EFFECTS OF F/T WTRs ON FERTILITY AND TRACE METALS IN SOILS

Total phosphorus concentration in WTRs was not decreased due to the F/T process, although the TKN was significantly decreased. The addition of WTR to soil decreased the concentration of plant available phosphorus in the soil. Phosphorus addition may need to be implemented when using WTRs in land application procedures.

Aluminum was not released in detectable amounts. Since aluminum is phytotoxic, it is important to know whether it leaches from WTRs. Cadmium, likewise, was not detected in leachate waters.

In most cases, the release of copper from soil-WTR(F/T) was indistinguishable from the columns containing soil only. While more zinc eluted from the soil-WTR(F/T) than from soil alone for residuals A,B and C, less zinc eluted from these mixtures than from soil-WTR(wet) mixtures. For residual D (shown in Figures 1 and 2), more zinc eluted from the soil-WTR(wet) than from the F/T residual

Metals leaching is not likely to cause problems when using F/T WTRs for land application processes. However more research is needed in this area. The total mass of a metal contained in a WTR or WTR-soil mixtures was not a uniform indicator of the leachability of that metal. More work on the extraction procedures used for determining metal species is needed to fully understand the mechanism of metals leaching from these materials.

## REFERENCES

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## FUNDING SOURCE

The work on NJ WTRs was funded by the A-280 Safe Drinking Water Program. A full NJDEPE/DSR technical report on this project can be ordered (609-292-9373). General information about the environmental research program at the Division of Science and Research is available (609-984-6070). DSR Reference No. 9400 .

Eileen Murphy is a Research Scientist with the Division of Science and Research.

Brian Dempsey is an Associate Professor of Environmental Engineering at The Pennsylvania State University. Mark Lunetta and Steven Elias were graduate students working with Dr. Dempsey at the time of this writing.

At the time of the project, James DeWolfe was an engineer with the American Water Works Service Co.. He is now a process engineer with Gannett Fleming, Inc.

Table 1. Summary of Water Treatment Residuals

WTR	State	Water Source	Treatment Process
A*	NJ	river & canal	conventional using alum
B*	NJ	reservoir	conventional using PACI <sup>1</sup>
C	NJ	reservoir	solids contact with alum, PAC <sup>2</sup> , lime, cationic polymer, filtration
D*	NJ	reservoir	preozonation, alum plus cationic polymer (CuSO <sub>4</sub> algal control in reservoir)
E	NJ	groundwater	Fe removal by chlorine oxidation, polymer addition for settling
F	PA	lake	alum charge neutralization, upflow filtration
F	PA	drainage stream	KMnO <sub>4</sub> oxidation, alum, lime, Calgon™ non-ionic polymer
G	PA	stream	conventional using alum/lime, PAC

<sup>1</sup> PACI = poly-aluminum chloride

<sup>2</sup> PAC = powdered activated carbon

\* Residuals used in field freeze/thaw experiments

