

Water Resources Research Institute

Annual Technical Report

FY 2002

Introduction

The Alabama Water Resources Research Institute is an interdisciplinary research center that was founded to help chart the new course toward solving existing and potential water resources problems.

The Institute's mission is to find ways to better use, manage and preserve water resources in Alabama, the Southeast and nationwide, and to disseminate that crucial information to the masses.

While water resources research began steadily increasing in the 1960s, much of the activity through the years was fragmented. Since its establishment in 1964, the Alabama Water Resources Research Institute has given a cohesiveness to this research, bringing together research faculty from various disciplines and universities to collaborate on water resources projects.

The Alabama Water Resources Research Institute, in partnership with state and federal agencies, the public and private sector, and the research universities throughout our state, continues the creed of research, education, and information dissemination. The Institute program financially supports and coordinates project teams, programs, and specialized centers, creating a unique opportunity for water resources research and education through multi-disciplinary approaches. This coordination of interdisciplinary fields brings together academia, state and federal agencies, and public/private organizations to investigate water resources problems. The Institute program doesn't merely promote and encourage water resources research; it supports the research, both financially and administratively. Funding from the Institute is used either as direct support for projects or as matching funds to help attract research support from state and federal agencies or the private sector. Without proper funding an Institute program cannot be as effective in administering to the needs of their individual state as well as the nation.

Priority research needs at the state, regional and national levels, along with the interests and expertise of research faculty, determine where the Alabama Institute targets its funding. Through the Institute, Alabama has become a home to strong research projects on many fronts, including water quality, policy and financing, groundwater hydrology and protection, toxicology, and acid rain impacts.

While work will continue in these areas, the Alabama Institute has expanded its research program into issues such as global climate change, non-point source pollution, bioremediation and geological information systems (GIS) technology.

In short, the Alabama Institute is positioned to bring about change for the future by discovering ways we can preserve and protect the earth and its resources, and do so in ways that take into account our economic, health, and societal needs. The Institute understands that water quality, economic viability, and community development are not mutually exclusive.

Research Program

Watershed Protection Through Building Material Substitution and Controlled Use

Basic Information

Title:	Watershed Protection Through Building Material Substitution and Controlled Use
Project Number:	2002AL1B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	Sixth
Research Category:	Water Quality
Focus Category:	Water Quality, Surface Water, Non Point Pollution
Descriptors:	Pollution Prevention, Stormwater Runoff, Watershed Protection, Building Materials
Principal Investigators:	Melinda Lalor, Shirley E. Clark

Publication

1. "Investigation of Wet-Weather Pollution Contributions from Building Materials Used at Industrial Sites." S. Clark, M. Lalor, R. Pitt, and R. Field. Proceedings of the 9th Annual Industrial Wastes Technology and Regulation Conference, San Antonio, Texas, April 13-16, 2003. Water Environment Federation, Alexandria, VA
2. "Wet-Weather Pollution Prevention through Materials Substitution as Part of Industrial Construction." S. Clark, M. Lalor, R. Pitt, and R. Field. Proceedings of the *th Annual Industrial Wastes Technology and Regulation Conference, Atlantic City, New Jersey, August 11-14, 2002. Water Environment Federation, Alexandria, VA

Watershed Protection Through Building Material Substitution and Controlled Use

Dr. Melinda Lalor and Dr. Shirley Clark

a. Problem and Research Objectives

Developmental pressures throughout the state of Alabama pose an increasing potential threat to sensitive watersheds. Areas such as the Lake Purdy watershed, which provides drinking water for much of the greater Birmingham area, and watersheds feeding tributaries and estuaries of Mobile Bay represent attractive building sites in rapidly developing areas of the state. If development is allowed to proceed in these areas, it is essential that it be carried out in ways that minimize the long term impact to the natural resources we depend on for drinking water, recreation and tourism, the seafood industry and commerce. Some sources of pollution linked to development, such as sedimentation during construction, are obvious. Others, such as the slow leaching of metals and organics from building materials, and their transport in the environment, are insidious, but perhaps no less important in the long run. If select building materials represent an important source of pollutants, reducing emissions at the source, through material substitution, will probably be more cost effective than attempting to treat stormwater runoff that has come in contact with these materials.

The objective of this research was to identify and quantify selected toxicants that are added to urban stormwater through contact with a variety of building materials. This information will be used to analyze the potential pollution prevention benefits and economic impacts associated with building material substitutions in sensitive watersheds.

b. Methodology

Aggressive and mild leaching tests were conducted on a variety of construction materials. The initial tests were gross leaching tests using a modified toxic characteristic leaching procedure (TCLP). Triplicate tests were made for each material, using the most aggressive water conditions to which they may likely be exposed. Water samples were analyzed for an extensive list of chemicals, including common constituents (pH, conductivity, TDS, total solids), nutrients (nitrates and phosphates), COD, heavy metals (including copper, zinc, lead, cadmium, chromium, and aluminum), organic compounds (especially the base-neutrals including: PAHs, phthalate esters, and phenols) and toxicity (using the Azur Microtox screening procedure). Results from these tests were used to determine the relative potential of each tested material for contributing runoff pollutants, and to provide a comprehensive list of the potential pollutants associated with the various materials tested. This information was used to direct the selection of materials and laboratory analyses for the second set of tests.

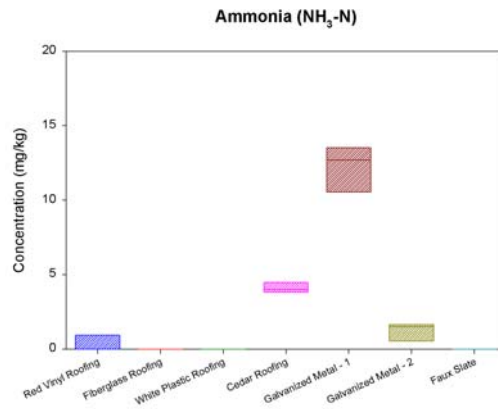
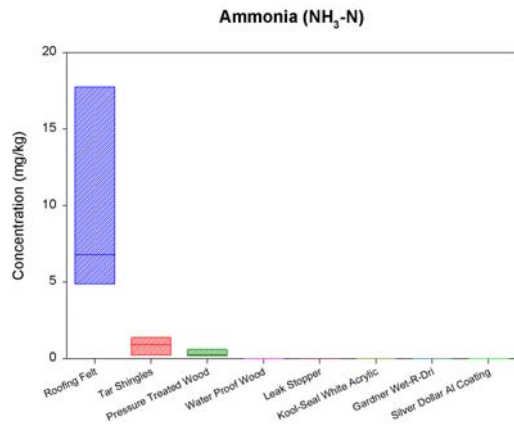
The second set of tests determine pollutant releases from a sub-set of construction materials under field conditions. These tests quantify the likely pollutant concentrations expected when the selected materials are exposed to actual weathering and rainfall conditions. Rainfall runoff from the materials is being collected and analyzed as the material ages. The chemical analyses conducted on runoff from each material are based on pollutants identified in the initial tests.

c. Findings and Significance

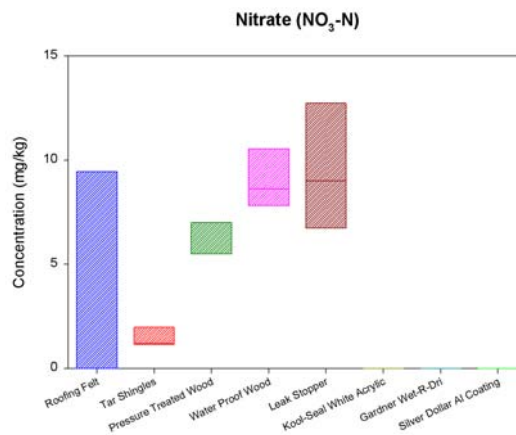
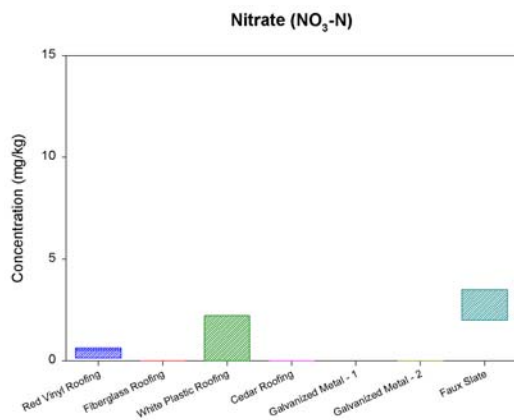
The results of the modified TCLP test are shown in Figures below. Results of particular interest include evidence of elevated levels of phosphate, nitrate and ammonia in runoff following exposure to common roofing and siding materials, resulting in an unexpectedly high

eutrophication potential. Elevated levels of semi-volatile organics and metals are also of concern due to potential for ecological toxicity. The samples are currently undergoing metals analysis.

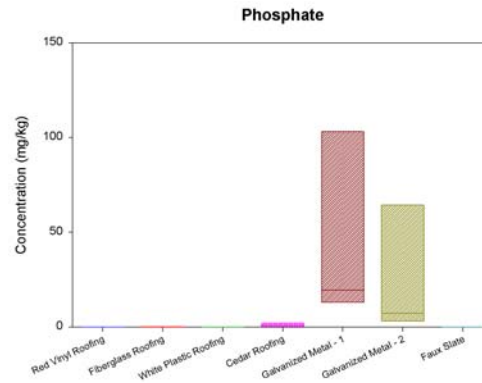
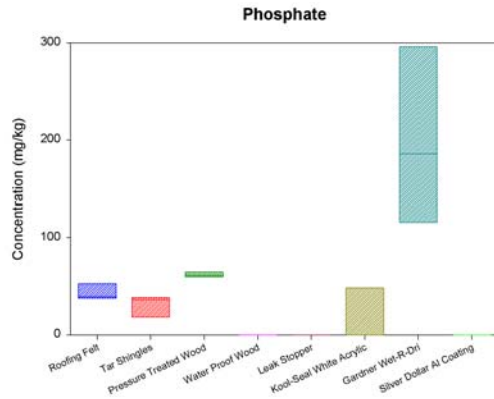
The results for the ammonia show that the first test of the galvanized metal contributed 11 – 14 mg/kg. Testing on roofing felt showed that it leached 5 – 15 mg/kg, indicating that the roofing felt would leach ammonia into the rainwater under the right conditions, but that the amounts would be highly variable.



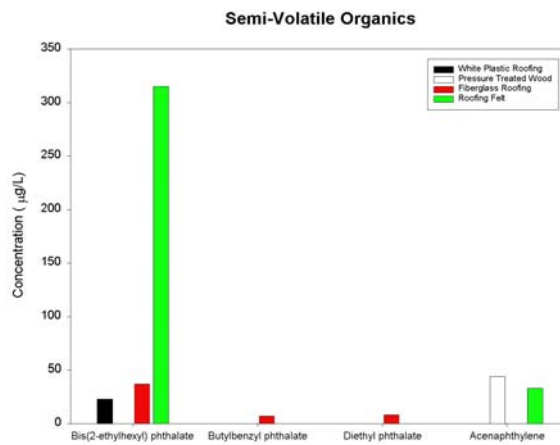
Testing for nitrate showed that nitrate was contributed from a variety of sources, including the roof patching compound “Leak Stopper.”



The phosphate results indicate that the galvanized metal roofing is a potential source of phosphate in runoff. Metal roofing leached between 5 and 75 mg/kg. In addition, several of the roof-patching compounds have the potential to leach phosphate into stormwater runoff. In particular, the Gardner Wet-R-Dri compound has the potential to release a significant amount of phosphorus (up to 300 mg/kg).



Organic results indicate that very few organics were seen in the leachate. The organic compound seen in the greatest concentration was bis(2-ethylhexyl) phthalate, a plasticizer in the roofing felt.



Preliminary results have shown that galvanized aluminum roofing has contributed the greatest concentrations of the pollutants of interest – conductivity, cations, and nutrients. Metals results are not available yet; however, the galvanized roofing is expected to contribute a significant metals load also. Other roofing materials that have been investigated to date appear to be leaching the phthalate esters from the plasticizers. In general, nutrient leaching from construction materials has not been investigated. The preliminary results of this project demonstrate that nutrient leaching may be significant in the right environmental conditions. The galvanized aluminum roofing had comparatively elevated concentrations of phosphate and nitrate in the leachate. Potential testing for environmental compatibility should include a wide range of potential pollutants, rather than simply focusing only on the expected organic and metallic pollutants.

Treatment of Heavy Metal-Contaminated Runoff Using Straw Coated with Sulfide

Basic Information

Title:	Treatment of Heavy Metal-Contaminated Runoff Using Straw Coated with Sulfide
Project Number:	2002AL4B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	Sixth
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Water Quality, Surface Water
Descriptors:	Runoff, Heavy Metals, Iron, Sulfide
Principal Investigators:	Robert W. Peters, Joseph J. Gauthier

Publication

1. Reters Robert W., S. Nunez, L.A. Blankinship, and J. Gauthier, 2003. "Stability of Straw Coated With Sulfide and Used for Treatment of Heavy Metal-Contaminated Runoff", in Conference Proceedings: Green Chemical Engineering Topical Conference, National AIChE Meeting, New Orleans, LA, pp. 139-151.

“TREATMENT OF HEAVY METAL-CONTAMINATED RUNOFF USING STRAW COATED WITH SULFIDE”

a. A statement of the problem and research objectives:

Runoff from construction sites, roofs, and roadways is known to contain heavy metals as trace contaminants, and can effect the bioecosystems near these runoff sites. Urban stormwater runoff has been recognized as a substantial source of pollutants to receiving waters [Davis et al., 2001]. Urban settings are a focal point for environmental contamination due to emissions from industrial and municipal activities and the widespread use of motor vehicles [Callender and Rice, 2000]. During storm events, a considerable increase in the concentrations of particle number, suspended solids mass, organic carbon, iron, and zinc have been observed in runoff streams [Characklis and Wiesner, 1997]; the concentration of zinc in runoff was highly correlated with organic carbon and iron exists primarily in the macrocolloidal fraction. Hares and Ward [1999] studied the concentration of motorway-derived contaminants including V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, Sb, and Pb, were measured in unfiltered stormwater collected during the initial stages of storm events. Higher levels of motor-derived heavy metal contamination exists in stormwater runoff from road sections with a higher average daily traffic density. The transport of anthropogenic constituents by runoff from urban roadways can adversely impact the quality of adjacent receiving waters and soils [Sansalone et al., 1996]. Heavy metal elements are the most persistent constituents found in pavement runoff [Sansalone et al., 1996]. Legret and Pagotto [1999] conducted a study investigating the quality of pavement runoff water from a 275-m motorway section over a one-year time frame, during which 50 rain events were sampled. Two different types of pollution were revealed; the first type was identified as chromic pollution and included suspended solids, chemical oxygen demand, total hydrocarbons, lead, and zinc. The second type of pollution was seasonal and incorporates chlorides, sulfates, suspended solids, and heavy metals due to the use of deicing salt in the wintertime. Runoff from roads have negative effects on biotic integrity in both terrestrial and aquatic ecosystems [Trombulak and Frissell, 2000]. Roads affect soil density, temperature, soil water content, light levels, dust, surface waters, patterns of runoff, and sedimentation, as well as adding heavy metals (especially lead), salts, organic molecules, ozone, and nutrients to roadside environments [Trombulak and Frissell, 2000]. The runoff chemistry from uncontrolled discharges of highway runoff can significantly impact receiving water quality and may require remediation by appropriate stormwater best management practices [Marsalek et al., 1997]. This project seeks to develop an efficient and low-cost technology to capture heavy metals from contaminated runoff, namely using straw that has been coated with sulfide compounds to bind the heavy metals to the straw.

The objectives for this research project are listed below:

- To determine whether sulfide adsorbed on the surface of straw/hay will serve as an effective binding agent/precipitation agent for removal of heavy metals from solution (e.g., run-off from sites);
- To identify preliminary conditions (e.g., pH, sulfide dosage/unit weight of straw, etc.) whereby heavy metals are effectively removed from solution;
- To determine adsorptive capacities of the heavy metals on the straw; and
- To determine the break-through characteristics of the heavy metals through the pack-bed straw reactors.

b. A brief explanation of methodology:

The scope of the research is three-fold: 1. Performing bench-scale batch isotherm characterization of the selected heavy metals onto straw and hay (both untreated and treated with sulfide compounds), 2. Performing continuous flow of heavy metal solutions through a packed-bed column containing straw, and 3. Modeling the bed depth-service time behavior of the heavy metal solutions through the columns to determine column breakthrough.

c. Principal findings and significance:

Isotherm experiments were performed in which different dosages of straw were subjected to different concentrations of heavy metal solutions (containing iron, cadmium, chromium, and lead). Results from these experiments are summarized in Tables 1 and 2. The adsorption/uptake of heavy metals onto the straw were modeled using the Langmuir and Freundlich isotherms:

$$\text{Langmuir: } q_e = \frac{Q^0 b C}{1 + bC} \quad \text{Freundlich: } q_e = K_N C^{1/n}$$

Table 1. Summary of Isotherm Parameters for Heavy Metal Adsorption onto Straw (Straw Dosage = 1.0 gm/L); pH ~ 2.2

Isotherm Model	Parameter	Heavy Metal			
		Iron	Cadmium	Chromium	Lead
Langmuir	Q ⁰ , (mg/g)	3.979	0.305	-0.281	1.116
	b, (L/mg)	0.234	0.587	-0.051	6.114
Freundlich	K _N	0.671	0.106	0.011	0.854
	1/n	0.567	0.4945	1.402	0.223

Table 2. Summary of Isotherm Parameters for Iron Adsorption Using Different Straw Dosages and Initial pH Levels.

Isotherm Model	Parameter	Dosage = 1.0 g/L		Dosage = 10.0 g/L
		pH ~ 2.6	pH ~ 4.05	pH ~ 4.1
Langmuir	Q ⁰ , (mg/g)	3.979	2.569	-5.244
	b, (L/mg)	0.234	0.172	-0.028
Freundlich	K _N	0.671	0.374	0.1545
	1/n	0.567	0.561	1.081

Straw is an excellent medium for constructing a barrier to urban and industrial runoff. It is readily available and relatively inexpensive. Straw also has the potential for chemical modification to increase its ability to remove pollutants such as heavy metals from runoff. Being a plant material, straw is potentially biodegradable. The rate and extent of biodegradation influences its usefulness as a pollution barrier, especially if it chemical modified to improve its ability to remove heavy metals and other pollutants.

Plant material such as straw consists primarily of two fractions, the readily biodegradable portion and the slowly degradable portion. The readily degradable fraction consists of small molecules such as sugars, amino acids, and metabolic intermediates that are present in the plant cells. It also includes macromolecules such as proteins, carbohydrates, lipids, and nucleic acids. These components are easily and rapidly degraded by microorganisms unless they are entrapped in cell-wall bound cells and are not accessible to microorganisms. The slowly biodegradable fraction consists primarily of plant structural polymers such as cellulose and lignin. These structures are degraded by microorganisms, but degradation is a slow process.

In this study, the rate of biodegradation of straw was determined. Four straw preparations were investigated: untreated straw, straw treated with sulfide, straw treated with iron, and straw treated with sulfide plus iron. Each of these straw preparations were packed into columns (50 grams of straw) and treated with water on a daily basis. The column experiments were performed in triplicate. After 1, 2, 4, 8, and 16 weeks, the columns were dissembled and samples (10 grams) prepared for analysis by blending to a fine powder. Each sample was treated with neutral detergent to extract the readily degradable fraction. Total loss of straw from the columns was determined by comparing initial and final weight of the straw at various times.

Total loss of straw. On average, about 10-15% of the total weight of the straw was lost during the first few weeks. Although the initial rate of loss of rapid, after 8 weeks, the rate of straw loss from the columns was significantly reduced. By week 16, ~25% of the total weight of the straw was lost. The rate of loss of straw treated with different chemicals appears generally similar, with the most rapid loss occurring during the first week. The heterogeneity of straw clearly limits the sensitivity of measuring the

neutral detergent fraction. Consequently, trends beyond those described above cannot be determined with certainty. For example, it appears that the loss of straw was reversed in S4, the straw treated with sulfide + iron, but this is unlikely. An increase in the biodegradable fraction would occur if there were microbial growth on an exogenous substrate, but none was provided in this experiment. The conclusions from this part of the study are that ~10% of the total straw is rapidly lost from the columns during the first 2 to 4 weeks, and an additional 15% is slowly lost during the next 8 to 12 weeks.

Biodegradability of the straw. Initially, ~42% of the straw was readily biodegradable, based on neutral detergent solubility. About half of this material disappeared within the first couple of weeks, leaving ~20% of the straw as “readily biodegradable”. These results are consistent with the pattern of total loss of straw during this early period. The most rapid loss of the readily biodegradable fraction occurred during the first two weeks, regardless of the type of treatment (untreated, sulfide, iron, or sulfide+iron). The remaining readily biodegradable material is probably entrapped within cells by cell walls that contain cellulose, and are not accessible to microbial degradation until the cellulose is degraded. Following the phase of rapid removal of biodegradable material, there appears to be a slight increase in the biodegradable fraction when looking at the pattern for the average biodegradability of the straw. This may be due to the accumulation of microbial biomass that is growing on the slowly degradable fraction (cellulose and lignin). Visual and microscopic observations revealed the presence of bacteria and fungi during this phase. The slight increase in biomass, due to the increase numbers of microbial cells, is too small to be reflected in the total loss of straw measurements. From examination of patterns of degradation for different straw treatments (untreated, sulfide, iron, and sulfide+iron), it is concluded that ~50% of the readily biodegradable portion of the straw is degraded during the first few weeks of exposure to water in columns. The straw then remains relatively stable for the remainder of the test period. If sulfide is bound to the readily degradable fraction (e.g., proteins) or retained in cells that become susceptible to biodegradation during the first few weeks, it would be rapidly lost. However, if the biodegradable fraction were removed by incubation of the straw in water, reagents might bind to the more slowly degradable fraction and therefore be more stable and provide longer functionality.

Use of Sonication/Acoustic Cavitation with Advanced Oxidants to Treat Petroleum Hydrocarbons Contaminated Surface Waters and Groundwaters

Basic Information

Title:	Use of Sonication/Acoustic Cavitation with Advanced Oxidants to Treat Petroleum Hydrocarbons Contaminated Surface Waters and Groundwaters
Project Number:	2002AL5B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	Sixth
Research Category:	Water Quality
Focus Category:	Treatment, Surface Water, Groundwater
Descriptors:	Sonication, Acoustic Cavitation, Advanced Oxidation, Groundwater, Surface Water, Petroleum Hydrocarbons
Principal Investigators:	Robert W. Peters, Joseph J. Gauthier

Publication

“USE OF SONICATION/ACOUSTIC CAVITATION WITH ADVANCED OXIDANTS TO TREAT PETROLEUM HYDROCARBONS-CONTAMINATED SURFACE WATERS AND GROUNDWATERS”

a. A statement of the problem and research objectives:

This project seeks to treat petroleum-hydrocarbon contaminated groundwater using a combination of sonication, vapor stripping, and advanced oxidants as a means to cleanup contaminated groundwater.

b. A brief explanation of methodology:

Four separate tasks are to be performed in this study. Batch and continuous flow experiments will be performed using sonication alone, vapor stripping alone, and combined sonication/vapor stripping. The study focused on treatment of benzene, toluene, ethylbenzene, and *o*-xylene (BTEX). Initial contaminant concentrations were generally held constant at 100 mg/L. The sonicator had an ultrasonic frequency of 20 kHz, and the power intensity was $\sim 38 \text{ W/cm}^2$. For those experiments involving air stripping, the air injection rate was normally held constant at 500 mL/min. Additional experiments were conducted for removal of benzene, toluene, ethylbenzene, and *o*-xylene, using different air flow rates, of 250, 500, 750, and 1,000 mL/min. Batch reaction treatments were operated for up to 10 minutes, with samples drawn for gas chromatography analysis every 2 minutes. Experiments were performed both in the absence and presence of advanced oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2). The project determined the removal of the parent petroleum hydrocarbon contaminant and identified and quantified any degradation products formed during the advanced oxidation treatment. As a part of the project, preliminary economic and process performance assessments were performed.

c. Principal findings and significance:

Results from air stripping treatment for 10 minutes are summarized below in Table 1. The results indicate that little improvement in terms of contaminant removal is achieved for air flow rates exceeding 500 mL/min. This flow rate was deemed to be the optimum air flow rate for the other experiments performed in conjunction with sonication.

Table 1. Summary of Results from Air Stripping Experiments.

Compound	Removal Efficiency, (%)			
	Air Flow Rate, (mL/min)			
	250	500	750	1000
Benzene	37.46	75.69	76.96	88.00
Toluene	39.98	77.34	78.09	83.51
Ethylbenzene	53.00	80.65	81.63	89.82
<i>o</i> -Xylene	55.37	73.47	77.72	78.21

Table 2 summarizes the removal efficiency of benzene, toluene, ethylbenzene, and *o*-xylene obtained after 10 minutes treatment using various treatment technologies (sonication alone, air sparging alone, sonication+air sparging, sonication+UV light, and sonication+air sparging+UV light). The results are shown in Figures 1 and 2, below.

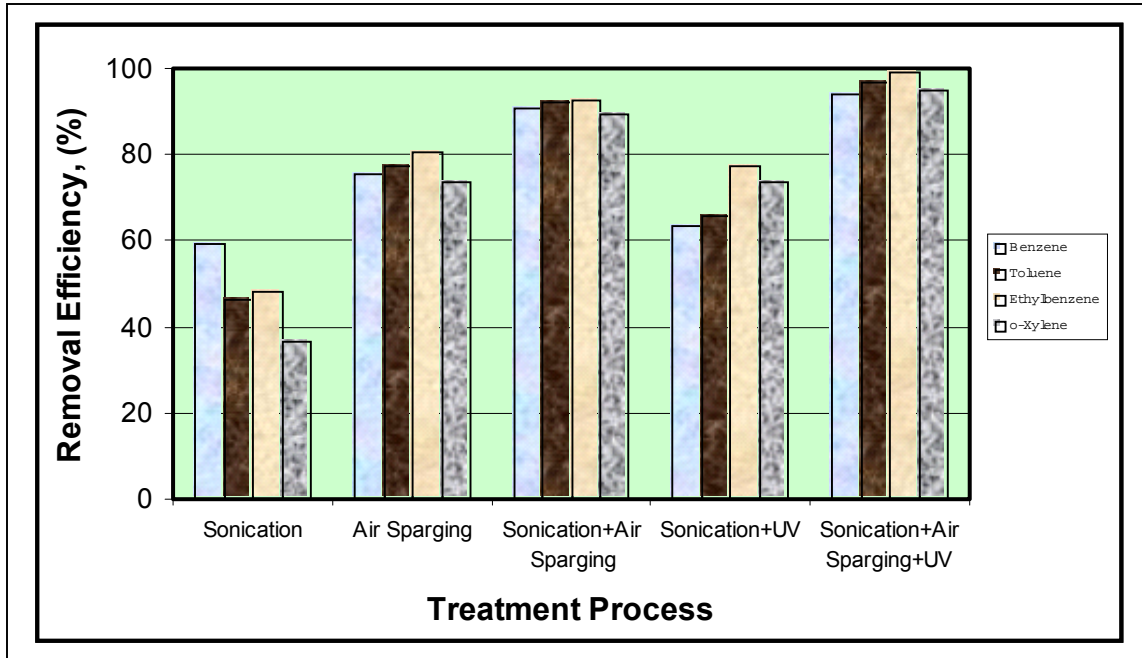


Figure 1. Comparison of Removal Efficiencies of BTEX Compounds Using Different Treatment Processes.

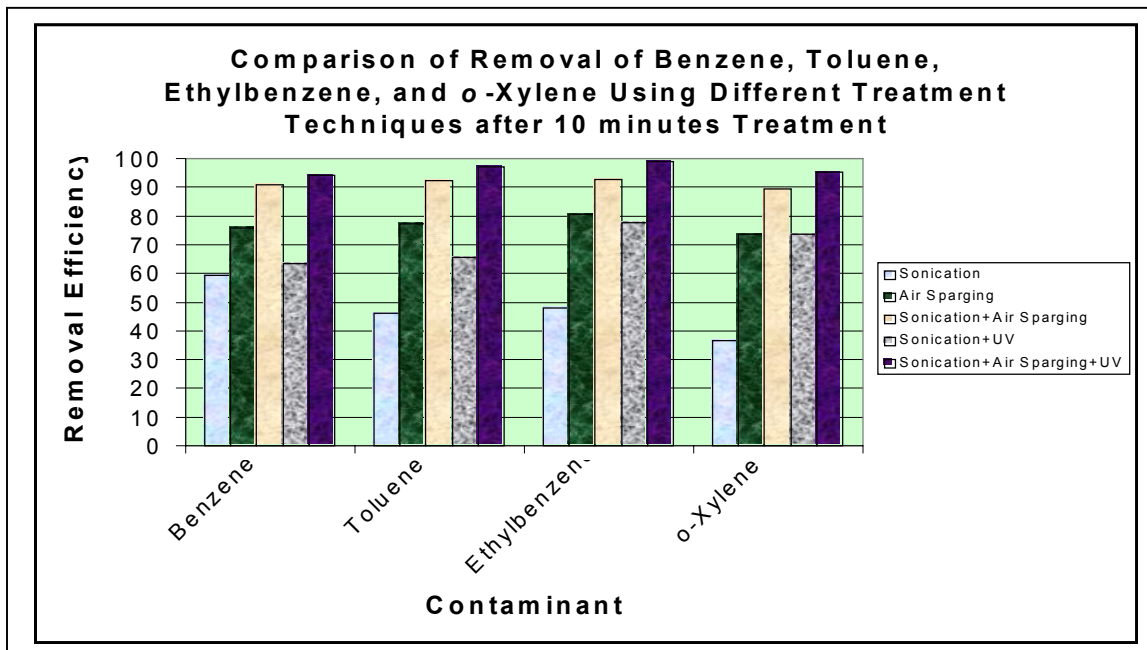


Figure 2. Comparison of Removal Efficiencies from Different Treatment Processes for BTEX Compounds from Solution.

The removals of benzene, toluene, ethylbenzene, and *o*-xylene obtained after 10 minutes treatment time using various treatment technologies (sonication, air sparging, combined sonication+air sparging, sonication+UV light, and sonication+air sparging+UV light) are summarized in Table 2. The removal of the BTEX compounds generally was in the order: sonication < sonication+UV light < air sparging < sonication+air sparging < sonication+air sparging+UV light. The highest removal efficiency was generally achieved for ethylbenzene, while the poorest removal efficiencies were achieved for benzene and *o*-xylene.

Table 2. Summary of Removal of BTEX Compounds Achieved after 10 minutes Treatment Time Using Various Treatment Technologies.

Compound	Removal Efficiency, (%)				
	Sonication	Air Sparging	Sonication+Air Sparging	Sonication+UV Light	Sonication+Air Sparging+UV Light
Benzene	59.170	75.685	90.765	63.469	94.029
Toluene	46.085	77.344	92.322	65.690	96.922
Ethylbenzene	48.020	80.647	92.755	77.521	98.889
<i>o</i> -Xylene	36.598	73.465	89.236	73.636	95.068

The effect of hydroxyl radical scavengers was addressed by adding 50 mg/L each of sodium carbonate and sodium bicarbonate to the solution containing 50 mg/L of benzene. After 10 minutes treatment employing sonication + air sparging, the removal efficiency of benzene decreased from 90.765% to 86.758% in the presence of the •OH scavengers, indicating the •OH scavengers had a minimal effect on removal of benzene using sonication + air sparging.

Information Transfer Program

USGS Summer Intern Program

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	3	0	0	0	3
Masters	2	0	0	0	2
Ph.D.	3	0	0	0	3
Post-Doc.	0	0	0	0	0
Total	8	0	0	0	8

Notable Awards and Achievements

Publications from Prior Projects

None