

REMOVAL OF PHOSPHATE AND WATERBORNE PATHOGENS FROM WASTEWATER EFFLUENT USING PERMEABLE REACTIVE MATERIALS

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ABSTRACT

Over the past decade, extensive laboratory testing and field studies have demonstrated the effective removal of phosphate from groundwater and wastewater using Basic Oxygen Furnace (BOF) slag, a waste material from the steel production process. The BOF slag contains significant concentrations of calcium and iron oxyhydroxides, which create high pH conditions following interaction with water. A laboratory column containing 10% BOF oxide by weight in silica sand has been operating continuously since 1993. With an influent concentration of approximately 3 mg/L PO₄-P, the column has discharged water containing less than 0.2 mg/L PO₄-P on a continuous basis. Two recent field applications have confirmed the removal of phosphate from domestic (North Bay, 1999) and communal (Massachusetts Alternative Septic System Test Center, October 2001) wastewater by BOF slag material. The applications have also demonstrated the capability of the treatment systems to remove waterborne pathogens, including coliform bacteria and *E. coli*, from the wastewater effluent. A second chamber containing organic carbon has been added to provide pH buffering of the effluent from the Cape Cod system.

RÉSUMÉ

Depuis une décennie, plusieurs tests en laboratoire et études de terrain ont démontré l'efficacité d'enlever les phosphates de l'eau souterraine ou usée par l'utilisation de scories de Fourneau à Oxygène Basique (FOB), un résidu provenant de la production de l'acier. Les scories de FOB contiennent des concentrations significatives en calcium et hydroxydes de fer qui créent des conditions de pH élevées suivant leur interaction avec l'eau. Une colonne de laboratoire contenant 10% de FOB par masse en sable siliceux a opéré en continu depuis 1993. Avec une concentration initiale d'eau d'environ 3 mg/L PO₄-P, la colonne a déchargé l'eau contenant une concentration inférieure à 0.2 mg/L PO₄-P sur une base continue. Deux applications de terrain récentes ont démontré le potentiel des scories de FOB pour soustraire les phosphates de l'eau domestique (North Bay, 1999) et usée de communauté (Massachusetts Alternative Septic System Test Center, October 2001). Les applications ont aussi démontré la capacité des systèmes de traitement de retirer les pathogènes transmissibles par l'eau comme les bactéries coliformes et *E. coli*, de l'effluent d'eau usée. Une deuxième chambre contenant de la matière organique fut rajoutée pour fournir un tampon pour l'effluent du système de Cape Cod.

1. INTRODUCTION

In situ treatment of dissolved contaminants in groundwater by permeable reactive barriers (PRBs) has developed as an effective and cost-efficient approach to the remediation and management of contaminated sites over the past decade (Blowes and Ptacek, 1992; Blowes et al., 1997; Powell et al., 1998). PRBs provide passive interception of contaminated groundwater and the destruction or removal of the contaminants by a combination of physical, chemical or biological processes within or down-gradient of the reactive materials. O'Hannesin and Gillham (1998) and Yamane et al. (1995) applied PRBs containing zero-valent iron for the treatment of chlorinated solvents in groundwater. Blowes et al. (1999abc) used zero-valent iron in a PRB to remove chromium (VI) and chlorinated solvents from groundwater prior to its discharge to a river. Benner et al. (1997; 1999) used organic carbon in a PRB to enhance the activity of

sulfate-reducing bacteria and promote the treatment of an acid-mine drainage plume from sulfidic mine tailings through the precipitation of metal sulfide minerals and the generation of alkalinity. Robertson et al. (2000) used similar organic reactive materials to effectively remove nitrate by promoting microbially mediated denitrification in groundwater impacted by domestic septic systems and agricultural wastes.

Baker et al. (1998) and Blowes et al. (1999; 2000) recognized the potential for Basic Oxygen Furnace (BOF) slag to remove contaminants such as phosphate, arsenic and selenium, and water-borne bacteria and viruses from groundwater. BOF slag is a poorly sorted mixture of material ranging in grain size from silt to fine gravel, and is a non-metallic waste byproduct of steel production, and is generated at several steel plants throughout North America. BOF slag contains various oxides and silicates of iron, calcium, magnesium and aluminum, but in

particular is rich in iron and calcium oxyhydroxides. Typically, the interaction between BOF slag and water results in elevated pH conditions of as high as 12, but no other measurable water quality impacts. Proctor et al. (2000) identified antimony, cadmium, total chromium, manganese, molybdenum, selenium, silver, thallium, tin and vanadium at concentrations in excess of background soil in the United States in samples of BOF slag as part of a review of 58 active steel mills. Toxicity Characteristic Leaching Procedure (TCLP) tests using leach solution at pH 2.8 for their samples generated leachate from BOF slag of non-hazardous characteristics. BOF slag is inexpensive and shipping and transport have a strong influence on its overall cost. BOF slag is commonly used as aggregate in roadbed and other construction projects.

McRae et al. (1999) evaluated BOF slag and other reactive materials for the treatment of arsenic and selenium in groundwater. Both arsenic and selenium were removed to very low levels for more than 125 pore volumes of flow in a dynamic test of a column that contained a mixture of silica sand, limestone and 10% BOF oxide by weight. The influent concentration of total arsenic (1:1 ratio of As(III) and As(V)) was 1 mg/L. Arsenic was non-detectable in the effluent (<0.018 mg/L). In a subsequent unreported column test conducted at the University of Waterloo (UW), BOF slag in a 1:1 mixture with gravel decreased concentrations of arsenic from 4 mg/L in the influent to less than 0.01 mg/L in the effluent. The test was conducted using low pH (<4) groundwater from an industrial site in the eastern United States. In the early summer of 2002, construction for the installation of a full-scale BOF-slag PRB for the treatment of arsenic in groundwater was initiated at an industrial site in the central United States.

This paper will focus on the use of BOF slag in PRB systems for the treatment of phosphorus and waterborne pathogens in groundwater. The work was initiated in the laboratory in the early 1990s, and has expanded to include several field-scale applications, some of which are active.

2. PHOSPHATE AND WATER-BORNE PATHOGENS IN GROUNDWATER

Phosphorus is an important constituent of domestic and agricultural wastewater. Concentrations of phosphate in wastewater may range between 5 and 15 mg/L PO₄-P. The natural capacity of subsurface soil and rock materials to attenuate the mobility of phosphate is limited. Thus, phosphate can be a mobile contaminant in groundwater. This mobility is a particular concern where domestic-wastewater or agricultural organic-waste systems are located in close proximity to surface water. Groundwater discharge or surface runoff can contribute phosphate loading to the receiving surface water. Phosphate is typically the limiting nutrient present in surface water. Increased inputs of phosphate can increase the growth of algae and other plants and upset the ecological balance of aquatic habitats.

Domestic wastewater and agricultural wastes are prevalent sources of bacteria and viruses in groundwater. The site-specific conditions and hydrogeologic setting associated with the introduction of wastewater to the subsurface have strong influences on the potential survivability and transport distance of pathogens in the subsurface. For example, Bales et al. (1995), in a controlled tracer test in a sand aquifer in Cape Cod, found detectable concentrations of bacteria persisting for tens of metres down-gradient of a source, but detectable virus concentrations were restricted to within several metres of the source. DeBorde et al. (1998), however, found transport distances for both bacteria and viruses of several tens of metres from a school septic system in a sand and gravel aquifer. Survival times of more than nine months for the viruses were also reported. The potential impact of water-borne pathogens is a particular concern in areas of groundwater use for water supply purposes (US EPA, 2000).

3. PHOSPHATE TREATMENT

Baker et al. (1998) evaluated the removal of phosphate from water by a variety of metal oxides in laboratory batch experiments. The metal oxides included BOF oxide, BOF slag and activated alumina. In batch tests, the oxides were incorporated in reactive mixtures containing 50 wt% silica, 45 wt% crushed limestone and 5 wt% metal oxide. Approximately 50 g of each reactive mixture in 500 mL solutions caused concentrations of phosphate to decrease from approximately 10 mg/L PO₄-P to less than 0.01 mg/L mg/L PO₄-P in periods of several hours.

On the basis of the batch-test results, dynamic column tests were initiated. Two columns containing the BOF oxide, crushed limestone and silica sand mixture and activated alumina, crushed limestone and silica sand mixture in the same proportions as in the batch tests were set up. Flow to the BOF oxide column averaged 1.3 pore volumes per day, and the residence time for water in the column was approximately 0.9 days. Flow to the activated alumina column was approximately 0.6 pore volumes per day, with an average residence time of approximately 1.7 days. The influent concentration of phosphate was approximately 3.3 mg/L PO₄-P.

The activated alumina column removed phosphate to concentrations of less than 0.01 mg/L PO₄-P for a period of two years (approximately 400 pore volumes) beginning in 1995. The pH of the effluent increased from approximately 7.5 to 9 during this period. Although the column provided excellent treatment performance, the potential utility of activated alumina in field applications is limited because of costs. Grain-surface analysis indicated the removal of phosphate by activated alumina was attributed to sorption (Baker et al., 1998).

Flow to the BOF oxide column was initiated in 1993. The pH of the effluent was initially 9.75, but decreased to approximately 9 after 1,450 pore volumes of flow in mid-1997. Removal of phosphate by the BOF oxide column to

concentrations of less than 0.01 mg/L PO₄-P was achieved at early time, but effluent concentrations of phosphate increased to less than 0.4 mg/L PO₄-P after 40 pore volumes of flow. After four years of continuous flow the BOF oxide mixture removed in excess of 80% and typically achieved 90% removal of the influent phosphate. Mineralogical analysis on samples of the reactive solids attributed the removal of phosphate by BOF oxide to sorption and the subsequent precipitation of low solubility calcium-phosphate minerals such as hydroxyapatite. A salt-tracer test confirmed there was no apparent change of the hydraulic characteristics of the material of the column after four years of treatment. After approximately eight years and 2,900 pore volumes of flow in early 2002, the effluent from the BOF oxide column continued to have a pH of 9.2 and a phosphate concentration of 0.3 mg/L PO₄-P or less.

Flow of 0.7 to 0.9 pore volumes per day was initiated in a third column containing a mixture of silica sand (40 wt%), limestone (35 wt%) and BOF slag (25 wt%) in 1994. Flow to this and the BOF oxide column has been maintained continuously to the present. The effluent from the BOF slag column had a pH of 10.85 and a phosphate concentration of less than 0.1 mg/L PO₄-P after approximately 1,500 pore volumes of flow in early 2002. The peak concentration of phosphate in the effluent from the BOF slag column was 0.5 mg/L PO₄-P, but this level of phosphate in the effluent was not persistent.

4. INITIAL FIELD TRIALS

Baker et al. (1997) evaluated the use of BOF oxide for the removal of phosphate in two field trials. In the first, a stream of effluent from the primary clarifier of a municipal sewage treatment plant was directed through a cylindrical column (0.5 m in diameter and 0.5 m in height) containing a mixture of BOF oxide, limestone and silica sand. The clarifier effluent had been pretreated by an oxidizing biofilter. Under flow rates of approximately 0.75 pore volumes per day, effective phosphate removal was attained for four months. Concentrations of total and orthophosphate in the influent were 3.93 and 2.5 mg/L PO₄-P, respectively. Average concentrations in the effluent were 0.14 mg/L (Total-P) and 0.05 mg/L (Ortho-P), indicating treatment efficiencies of in excess of 95 % removal.

In the second trial, the BOF oxide mixture was incorporated in the treatment chamber of a funnel-and-gate system that intercepted the plume from a septic system at a rural school. The treatment chamber was 2.0 m in width in the direction perpendicular to groundwater flow, 0.7 m in thickness, and 1.0 m in depth, and was installed at and below the water table. Monitoring indicated that there was some variability in the groundwater flow characteristics in the vicinity of the system and the concentration of phosphate entering the treatment chamber. The BOF-oxide mixture reduced phosphate concentrations from as much as 2 mg/L PO₄-P

in the influent to approximately 0.2 mg PO₄-P within the treatment chamber.

5.0 CURRENT FIELD DEMONSTRATIONS

BOF slag has been used in several systems to remove phosphorus from wastewater since the initial demonstrations. These demonstrations have included septic systems for single-family households, or equivalent, and communal systems for rural hotels and campground facilities. The BOF slag is mixed with gravel or crushed stone to generate a material with a hydraulic conductivity of more than 10⁻² cm/sec.

A BOF slag treatment chamber was installed as part of the septic system at a single-family household in North Bay, Ontario in the fall of 1999. The effluent from the septic system is treated in an oxidizing sand filter. Ammonia is converted to nitrate and the organic content of the wastewater is decreased in the sand filter. The effluent from the sand filter is captured and introduced to the BOF slag chamber, which contains a 1:1 mixture of BOF slag and gravel. The effluent from the BOF slag chamber is discharged through screened pipes to the vadose zone. The water table occurs at a depth of approximately one metre below ground surface in the vicinity of the infiltration gallery. The temperature, pH, phosphate and e-coli content of the effluent from the septic system, sand filter and BOF chamber have been monitored once or twice a month by the City of North Bay, on behalf of the Ontario Ministry of Environment. Monitoring results as a function of time are shown on Figures 1a-d. Temperature is similar in all components of the wastewater treatment system, and reflects seasonal variations of air temperature. The pH of the effluent from the BOF slag chamber has consistently been above 12. The results indicate sustained and excellent removal of phosphorous and waterborne pathogens from the septic system effluent by the BOF slag chamber. Phosphate in the effluent from the BOF chamber has been less than 0.05 mg/L PO₄-P. E. coli have been non-detectable (less than 5 or 20 CFU (Colony Forming Units)/ 100 mL) in all but one sample. No special maintenance of the BOF slag chamber has yet been required. The pH of the shallow groundwater in three monitoring wells approximately a meter down-gradient of the infiltration gallery ranged from 6.24 to 6.93 seven months after the system was installed. The pH buffering has been achieved through geochemical interactions with the aquifer materials and CO₂ in the vadose zone in the vicinity of the infiltration bed. This observation is consistent with that observed at the zero-valent iron PRB in Elizabeth City (Blowes et al., 1999b). Monitoring of that PRB system has shown that buffering of the elevated pH (>10) conditions created by zero-valent iron to background levels occurs in the groundwater within transport distances of several meters down-gradient of the barrier.

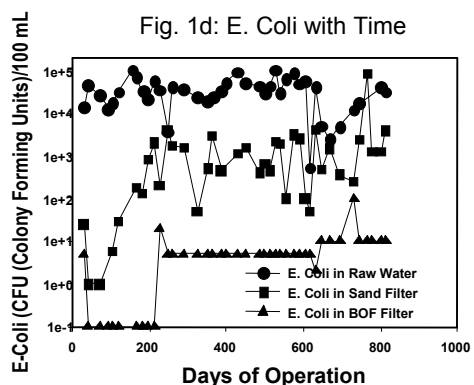
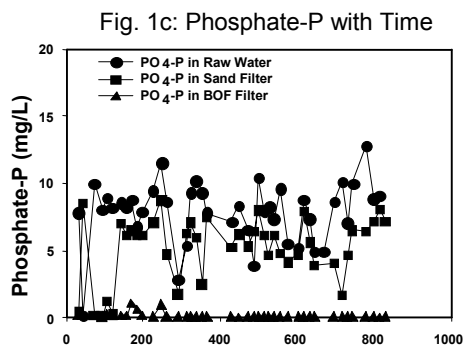
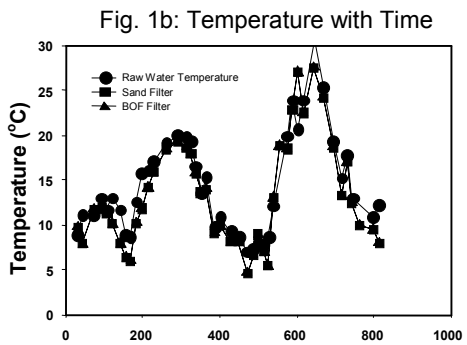
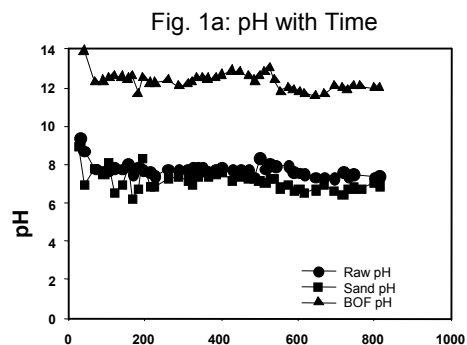


Figure 1: Monitoring data as a function of days since operation of a domestic system for a single-family residence was initiated. The data represent effluent from the septic tank (raw water), effluent from the aerobic sand filter (sand filter) and effluent from the BOF-slag filter (BOF filter). The data include pH (Figure 1a), temperature (Figure 1b), phosphate (Figure 1c) and E. coli (Figure 1d).

At the Massachusetts Alternative Septic System Test Center, a BOF-slag chamber (Phosphex™) was installed in October 2001. The BOF slag is enclosed in a concrete tank. The chamber receives approximately 330 U.S. gallons (1,240 L) of communal wastewater that has been aerobically pre-treated daily. The wastewater has a residence time of approximately a day in the chamber. The wastewater has a BOD₅ between 3 and 7 mg/L, pH of 7 and phosphate (as PO₄) of 3.75 mg/L. E. coli are present at between 1,000 and 20,000 CFU/100 mL. The pH of the effluent has ranged from 11.53 to 11.97, but is gradually decreasing with time. Phosphate concentrations in the effluent have been non-detectable (<0.05 mg/L as PO₄). Total phosphorus has also not been detected in the effluent (< 0.025 mg/L P). E. coli have also not been detected in the effluent (<5 CFU/100 mL). The elevated pH of the effluent has been identified as a concern for discharge to surface water, and to groundwater in some jurisdictions, therefore a second chamber was added to the treatment system in June 2002 to evaluate approaches to buffer the effluent pH.

6. SUMMARY

BOF slag is an effective material for use in PRB systems for the removal of phosphorus and pathogens such as E. coli from groundwater and wastewater. Laboratory columns containing BOF oxide have provided sustained removal of phosphorus for a period of more than eight years. At the field-scale, BOF slag and gravel mixtures have achieved removal of phosphate to concentrations of less than 0.05 mg/L PO₄-P, and the removal of E. coli in wastewater from domestic septic-system effluent to non-detectable levels (<5 CFU/ 100 mL). The excellent treatment levels could provide significant benefits in decreasing the negative impacts of on-site wastewater treatment systems on groundwater and receiving surface water systems. The

BOF slag is generated at several steel-production facilities in North America. The cost of BOF slag is comparable to that of typical construction aggregate materials. The combination of excellent treatment potential and inexpensive cost makes BOF slag a good candidate for *in situ* treatment of selected contaminants in groundwater. Although the tendency for BOF slag to generate effluent with elevated pH precludes its use in treatment systems that discharge directly to surface water, buffering of the pH to background levels can be achieved within short transport distances in situations where discharge to the subsurface is feasible. Alternately, pH buffering of the effluent could be achieved in an additional treatment chamber prior to discharge to surface water or groundwater.

7. REFERENCES

Baker, M.J., D.W. Blowes and C. J. Ptacek, 1997. Phosphorus adsorption and precipitation in a permeable reactive wall: applications for wastewater disposal

- systems. *Land Contamination and Reclamation* **5**(3): 189-194.
- Baker, M.J., D.W. Blowes and C. J. Ptacek, 1998. Laboratory development of reactive mixtures for the removal of phosphorus from onsite wastewater disposal systems. *Environmental Science and Technology*, **32**(15): 2308-2316.
- Bales, R.C., Shimin Li, Maguire, K.M., Yahya, M.T., Gerba, C.P., and Harvey, R.W., 1995. Virus and bacteria transport in a sandy aquifer, Cape Cod, MA. *Ground Water* **33**(4); 653-661.
- Benner, S.G., Blowes, D.W. and Ptacek, C.J. 1997. A full-scale porous reactive wall for prevention of acid mine drainage. *Ground Water Monitoring and Remediation*, **17**(4), 99-107.
- Benner, S.G., D.W. Blowes, W.D. Gould, R.B. Herbert Jr., and C.J. Ptacek 1999. Geochemistry of a reactive barrier for metals and acid mine drainage. *Environmental Science and Technology*, **33**; 2793-2799.
- Blowes, D.W., and Ptacek, C.J., 1992. Geochemical remediation of groundwater by permeable reactive walls: Removal of chromate by reaction with iron-bearing solids. In *Proceedings of the Subsurface Restoration Conference*, Dallas TX, June 21-24. pp 214-216.
- Blowes, D.W., C.J. Ptacek and M. Baker, 1996. Treatment of wastewater. G.B. Patent 962338-7, filed November 11, 1996; Canadian Patent 2,190,038, filed November 11, 1996; U.S. Patent 08,745,734, filed November 12, 1996.
- Blowes, D.W., C.J. Ptacek and J.L. Jambor, 1997. In-situ remediation of Cr(VI) contaminated groundwater using permeable reactive walls: Laboratory studies. *Environmental Science and Technology*, V. **31** (12): 3348-3357.
- Blowes, D.W., Puls, R.W., Gillham, R.W., Ptacek, C.J., Bennett, T.A., O'Hannesin, S.F., Hanton-Fong, C.J., Paul, C.J. and Bain, J.G., 1999a. An *In-Situ* Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 1 Design and Installation. United States Environmental Protection Agency, Cincinnati, OH, Report EPA/600/R-99/095a.
- Blowes, D.W., Puls, R.W., Gillham, R.W., Ptacek, C.J., Bennett, T., Bain, J.G., Hanton-Fong, C.J., and Paul, C.J., 1999b. An *In-Situ* Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 2 Performance Monitoring. United States Environmental Protection Agency, Cincinnati, OH, Report EPA/600/R-99/095b.
- Blowes, D.W. and Mayer, K.U., 1999c. An *In-Situ* Permeable Reactive Barrier for the Treatment of Hexavalent Chromium and Trichloroethylene in Ground Water: Volume 3 Multicomponent Reactive Transport Modeling. United States Environmental Protection Agency, Cincinnati, OH, Report EPA/600/R-99/095c.
- Blowes, D.W., C.J. Ptacek, S.G. Benner, C.W.T. McRae and R.W. Puls 2000. Treatment of dissolved metals and nutrients using permeable reactive barriers. *Journal of Contaminant Hydrology* **45**: 123-137.
- DeBorde, D.C., Woessner, W.W., Lauerman, B., and Ball, P.N., 1998. Virus occurrence and transport in a school septic system and unconfined aquifer. *Ground Water*, **36**(4): 825-834.
- McRae, C.W.T., Blowes, D.W., and Ptacek, C.J., 1999. *In situ* removal of arsenic from groundwater using permeable reactive barriers: a laboratory study. Sudbury '99- Mining and the Environment II conference, September 13-17, 1999, Sudbury, Ontario, pp. 601-609.
- O'Hannesin, S.F. and Gillham, R.W. 1998. Long-term performance of an in situ "iron wall" for remediation of VOCs. *Ground Water*, **36**(1): 164-170.
- Powell, R.M., Puls, R.W., Blowes, D.W., Vogan, J.L., Gillham, R.W., Powell, P.D., Schultz, D., and Landis, R., 1998. Permeable Reactive Barrier Technologies for Contaminant Remediation. U.S. Environmental Protection Agency, U.S. Office of Research and Development, U.S. Office of Solid Waste and Emergency Response, EPA/600/R-98/125, 94p.
- Proctor, D.M., Fehling, K.A., Shay, E.C., Wittenborn, J.L., Green, J.J., Avent C., Bigham, R.D., Connolly, M., Lee, B., Shepker, T.O., and Zak, M.A., 2000. Physical and chemical characteristics of blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags. *Environmental Science and Technology*, **34**(8): 1576-1582.
- Robertson, W.D., Blowes, D.W., Ptacek, C.J. and Cherry, J.A., 2000. Long-term performance of in situ reactive barriers for nitrate remediation. *Ground Water*, **38**(5): 689-696.
- United States Environmental Protection Agency, 2000. 40 CFR Subpart S, Parts 141 and 142, RIN 2040-AA97 National Drinking Water Regulations, Ground Water Rule, Office of Water.
- Yamane, C.L., Warner, S.D., Gallinatti, J.D., Szerdy, F.S., Delfino, T.A., Hankins, D.A., and Vogan, J.L., 1995. Installation of a subsurface groundwater treatment wall composed of granular zero-valent iron. Extended Abstracts of The Symposium on Contaminant Remediation with Zero-Valent Metals, 209th National Meeting of the American Chemical Society, Division of Environmental Chemistry (April 2-7), Anaheim, CA, pp. 792-795.

