2001 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #96.

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TVA Research on Coal Combustion By-Products: Uses and Environmental Impacts

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KEYWORDS: coal combustion by-products, CCP, fly ash, scrubber gypsum, land application, mine land reclamation, agricultural application, arsenic, metals, CCP storage areas, disposal areas, leaching, groundwater

ABSTRACT

Scientists within the Tennessee Valley Authority (TVA) Air, Land & Water Sciences organization have performed research on coal combustion by-products (CCP) for a number of years through a variety of laboratory, greenhouse, and field projects. Research has focused on the benefits and environmental impacts of high-volume land application, practices to control environmental impacts of on-site storage, and on providing data that may affect current regulations or influence future legislation that governs off-site use or on-site storage of CCP. This paper highlights TVA's experimental and applied research on CCP including: 1) reactions of CCP in soil and water; 2) leaching of CCP constituents, particularly arsenic (As) and metals; 3) greenhouse plant uptake and yield studies; 4) mine land reclamation with co-mixed CCP and municipal biosolids and the effects on chemical and physical properties of mine spoil, environmental parameters, and sustainable vegetation; 5) agricultural applications of co-mixed biosolids and CCP on crop yield and metal and nutrient uptake; 6) vegetation and turf production on CCP storage areas using minimal amounts of soil in conjunction with compost and fertilizer; 7) accelerated weathering of CCP to predict As bioavailability; 8) ecological risk assessment, speciation, and fate of CCP-borne As; 9) impact of high-volume scrubber gypsum/fly ash application on groundwater quality; 10) reduction of ammonia (NH_3) loss and attenuation of phosphorus (P) and metals solubility by CCP during chicken litter composting; and 11) use of CCP to sequester carbon dioxide (CO_2) for algal biomass production and conversion to biofuels.

INTRODUCTION

The 11 operating fossil fuel plants in the TVA electric power system produce in excess of 6 million tons of CCP annually. A research program to evaluate CCP for potential uses and environmental impacts has been on-going at TVA's Environmental Research Center in Muscle Shoals, Alabama for a number of years. This research has been conducted in the laboratory, in greenhouse experimentation, and in a variety of field projects. The emphasis has been on reactions of CCP in the soil-water-plant system, and has included: 1) abandoned mine land reclamation; 2) agricultural uses for co-mixed CCP and municipal biosolids; 3) vegetation and turf production on dry stack ash storage areas; 4) co-composting of poultry litter (PL) with CCP to attenuate P, metals, As, and selenium (Se) solubility and reduction of nitrogen (N) losses due to ammonia (NH_3) volatilization during composting; and 5) the effect of high-rate scrubber gypsum (SG) soil applications on plant growth, metal uptake, and groundwater quality.

Current studies include: 1) use of accelerated weathering techniques on CCP and CCP-soil mixtures to predict future As bioavailability and leaching potential from storage areas; 2) speciation of As in CCP; and 3) use of CCP for carbon (i.e., CO_2) sequestration for algal biomass production and conversion to biofuels. A general discussion of some of the studies that have been conducted within these research areas follows below. Due to space limitations, detailed tabulated data have not been included, but additional information may be obtained from the author.

RECLAMATION

A three phase research project was undertaken to reclaim a 5-acre tract of highly acid (pH 2.7) barren mine spoil in northeastern Tennessee by use of co-mixed CCP and municipal biosolids. The environmental impact of the reclamation was assessed by monitoring heavy metal uptake by vegetation and leaching of by-product constituents from the treated soils. Emphasis was on metal equilibria and leachate chemistry to assess short- and long-term behavior of the biosolids-ash co-mixtures in soil.

Phase I involved collection and analysis of CCP from a TVA fossil plant in the area and biosolids from the city of Knoxville, TN. The biosolids were considered a "Class A" sludge, suitable for land application due to its low metal content. The material was especially suitable for land reclamation because of its relatively low calcium carbonate equivalent (39%) and the low amount of plant available nitrogen (PAN - 6 lb/t). The sludge could be applied at high rates - without undue concern for excessive nitrate (NO_3^-) leaching loss or overliming - which added a considerable amount of necessary organic matter to the barren spoil. The beneficial effects of the fly ash were potassium (K), additional micronutrients, and the physical conditioning effect of the ash on the heavy clay spoil.

Phase II consisted of laboratory characterization of co-mixtures for various chemical and physical parameters, including nitrogen mineralization potential and water-soluble constituents. Greenhouse testing of a wildlife grass/legume seed mixture for growth performance on various combinations and spoil application rates of CCP/biosolids co-mixtures was included in Phase II. The co-mixed materials appeared to provide more than adequate nutrition of the major elements, i.e., N, P, K, calcium (Ca), and magnesium (Mg), and micronutrients, i.e., boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn) while posing little risk for heavy metal accumulation in the plants. A cause for concern for wildlife would be Se accumulations in a field situation to levels which occurred in the plants after 5 weeks' growth (up to 167 mg/kg).

These concentrations may have been the result of readily plant available Se in the freshly applied material only, since Se uptake and concentration in plant tissue was essentially negligible with continued plant growth The results were used to formulate application rates for Phase III.

Phase III was the reclamation effort, which consisted of twelve 75'x25' experimental plots of 4 rates of biosolids/ash co-mixture imposed on part of the area. The application rates were a 1:1 mixture of 0, 30, 50, or 100 t/acre each of biosolids and ash. This provided an N rate of 0, 180, 200, and 600 lb/acre (6 lb plant available N/t biosolids). A blanket application at the 50 t/acre rate was made over the remaining area.

Observations three years after treatment applications showed elimination of acid run-off, complete erosion control, attenuation of inorganic and organic pollutants, and increased soil nutrient levels. The most profound effects occurred with the 100 t/acre rate.

AGRICULTURAL USE

In conjunction with the reclamation project, research demonstration projects were also conducted in the vicinity of three large municipalities in Kentucky and Tennessee (Site 1, 2, or 3) to evaluate the agricultural effectiveness of CCP-biosolids co-mixtures. The experimental protocol was identical among the four projects, i.e., laboratory characterization, followed by greenhouse evaluations, then field studies. Fly ash from two different TVA fossil plants (Ash #1 & Ash #2) was used in the mixtures at two of the sites, and a flue gas desulfurization product (FGD - limestone scrubber sludge) from another TVA fossil plant was used at the third site. Biosolids were collected from the respective communities.

All by-products were analyzed singly, in 1:1 co-mixtures, or in various co-mixture ratios mixed into soil for total concentrations of plant nutrients and heavy metals. The macronutrient content of the biosolids ranged from marginal to adequate for plant growth; metal concentrations were considered limiting under the lifetime (100 year) cumulative metal addition standard. The P content in the CCPs was low but Ca, K, and Mg were adequate, as was the micronutrient content. The As content of Ash #1 and the FGD scrubber sludge approached the ceiling limit of 41 mg/kg stipulated by State regulations. The same fly ash also exhibited elevated levels of water soluble As, Cu, and Ni. Boron and Mo were elevated in water extracts of fly Ash #2.

Bulk soil was collected from each site to test the growth and yield response of pasture grass, soybeans, and corn to CCP-biosolids mixtures in a series of greenhouse experiments. Co-mixture application rates varied by soil type and ranged from 2.5 to 35 t/acre. There was no response for wheat, and a positive response for grass and soybeans grown on amended soil from Site 1. The response for corn in this soil was positive at lower application rates, but negative at a high rate (35 t/acre). For Site 2 amended soil across all application rates, there was no treatment response for wheat, a positive response for grass, a mixed response for corn, and a negative response for soybeans. For Site 3 amended soil, there was a positive response for wheat, no response for corn, and a negative response for grass and soybeans. There was no evidence of metal toxicity in any plant species on any soil. However, symptoms of B toxicity were evident in early growth of corn on the Site 2 amended soil.

Extraction of soil from each site with DTPA-TEA after crop harvest indicated varying amounts of residual metals due to by-product additions. The concentrations were dependent both on soil type and on the type of by-product applied. There was little evidence to indicate that metals, As, or Se would be solubilized from the by-products once applied to soil, at least in the near term, to a degree sufficient to cause concern for natural water contamination.

VEGETATION OF DRY STACK FLY ASH DISPOSAL AREAS

Wind and water erosion of open, dry stack fly ash disposal areas are major problems at some fossil fuel plants. Consequently, frequent watering to allay dust, and repair of eroded and unstable areas constitute a major operation and maintenance (O&M) cost to the plant. Establishment of sustainable vegetative cover on such areas may remedy these problems. Such cover prevents dusting and reduces the need for watering other than for maintenance of the growing plants.

A research project was initiated to address these issues at a TVA fossil plant dry stack fly ash disposal area. This 70 acre area presented an environment that was essentially sterile, and was deficient in plant macronutrients although sufficient in essential trace elements. Due to the lack of macronutrients and microbial activity, the ash by itself represented a very poor environment for sustaining plant growth.

A series of greenhouse studies evaluated the establishment, survival rate, and growth of seeded warm and cool season grasses and legumes on the ash. Additions of soil, poultry litter (PL), composted poultry litter (CPL) with inorganic N and P fertilizers to the ash supported better and more diverse plant growth than did the fertilized ash alone, likely due to the introduction of an essential microbial population. The ash provided sufficient K for plant growth. Legumes grew better with soil and CPL amendments while grasses performed better with an amendment of un-composted PL and soil. Cool season plants generally grew faster than did warm season species.

Plant species that appeared promising were common bermuda grass, KY-31 fescue, white and yellow sweet clover, and Blackwell switchgrass, a renewable energy crop. The method of seed bed preparation was also shown to be important when establishing plants by seed, i.e., amendments were best mixed with a tillage practice to a depth of 5-6 inches for maximum growth rates and coverage. Mixing increases the water holding capacity of the ash to promote plant sustainability through a deeper rooting system, and also reduces salt damage to the germinating seed.

Turf grass sods also were tested for their potential as a vegetative cover and as a potential income source to TVA through sod production and sales. A hybrid bermuda sod (variety 419) grew much better than St. Augustine grass or zoysia. An amendment of soil plus composted poultry litter resulted in the best growth of these turf grasses.

Based on these results, a replicated field plot experiment was initiated on the disposal area to evaluate the performance of seeded bahia grass, common bermuda grass, weeping lovegrass plus switchgrass, and sodded bermuda, St. Augustine, and Zoysia grass on plots amended with soil, CPL or a combination of soil plus CPL. A microbial inoculant was applied to half of each plot.

On plots amended with soil or soil plus CPL, the growth of common bermuda was good, but the growth of bahia grass and the lovegrass/switchgrass combination was not. For the sod grasses, the hybrid bermuda outperformed St. Augustine grass and zoysia, with the growth of zoysia being very poor. How-ever, a hot and dry summer likely biased the results against the zoysia crop since this species is slower to establish and requires large amounts of water.

Large-scale planting (30 acres) of a winter cover, consisting of white sweet clover, KY-31 fescue, and unhulled common bermuda grass was conducted in early fall after site preparation with a minimal application (two inches) of topsoil, CPL at a rate of 5 t/acre, and phosphate fertilizer. Although bermuda grass is a warm season grass, the seeds over-wintered and germinated in the spring, thus eliminating an extra seeding step and reducing total costs of vegetation. Results were a sustainable vegetative cover which required minimal care except watering.

COMPOSTING OF CCP AND POULTRY LITTER

Composting is a viable option for the management and utilization of PL. However, limitations within the process are odor and excessive N loss due to NH_3 volatilization, while NO_3^- leaching and excess P and other elements (As, Cu, Se) may be problems associated with the final product. Co-mixing CCP, particularly fly ash, with PL during composting was shown to reduce NH_3 volatilization and N loss by serving as an adsorbing medium for ammonia. Amending PL with fly ash reduced cumulative NH_3 losses during composting from 30 to 54 percent over non-amended litter during a 24 week period. The mechanism was likely precipitation as ammonium sulfate. Scrubber gypsum was less effective than fly ash.

Reducing the nitrification rate of ammonium to NO_3^- in composting litter will conserve against NO_3^- leaching. Addition of fly ash reduced nitrification rates by 45 to 84%, depending on the amount of ash added. Adsorption of P by the oxidic components (Al, Fe, and Mn) of fly ash reduced P solubility in the PL by 14 to 64 percent. The alkaline, organic matrix of PL reduced the concentrations of water-soluble As in the ash, but the ash had no effect on reducing As solubility in PL. Reductions of 32 to 48 percent in Cu solubility were achieved with fly ash, but scrubber gypsum was ineffective. Se solubility was low in all cases.

HIGH VOLUME SCRUBBER GYPSUM SOIL APPLICATIONS

Risk assessment data which can delineate the potential for plant uptake and leaching of As from FGD by-products will help the U.S. Environmental Protection Agency formulate a reasonable policy for use or disposal of As-containing FGD and allay concerns of environmental groups. Accordingly, a three-year replicated plot field study was conducted wherein high rate applications of SG over a two-year period of 90 dry tons/acre/yr in combination with a total of 15 dry tons/acre of CPL were used to improve marginal soil for growth of alfalfa, wheat, and white clover. Conventional fertilizers were used as a control. The annual soil loading rate of As due to application of this FGD was up to 4.7 kg/ha (4.2 lb/acre) based on concentrations of As determined by laboratory analyses.

The objective of the study was to determine the effect of high soil application rates of SG on As and metal accumulation in soil, plants, and groundwater. The three year study consisted of three replications of cropping treatments within a 2.2 acre area. Periodic plant, soil, and water sampling monitored availability of FGD-borne As, metals, and nutrients to plants, and accumulation of metals and As in the soil and propensity for leaching. Wells were installed outside the plot area and suction lysimeters within the plot to monitor groundwater quality before, during, and after the study.

Overall, there was little adverse effect on plant growth due to high rates of FGD application. Arsenic concentrations were elevated in alfalfa grown on CCP-amended soil in 1995 and 1996, but not in 1997. The peak As concentrations in water collected at three feet beneath the plot surface by the lysimeters over a 2.5 year period were 63 µg/L in Fall 1995; less than 1 µg/L in Spring 1996; 77 µg/L in Winter 1996 after the second by-product application; 44 µg/L in Spring 1997; and 19 µg/L by Summer, 1997.

The rapid attenuation of As concentrations at three feet beneath the plot shortly after SG application indicated that leaching of As from the SG would not likely become a problem over time. Notably, As concentrations in groundwater remained below detection levels throughout the demonstration. Considering the amount of As applied, vertical movement of As from the plot was remarkably small, although several other parameters increased. This suggested that, under the conditions of this study, the form of As (likely Arsenate (V) as H_3AsO_4) in the most recent application governed As uptake by the plant and leaching through soil. Calcium arsenate [$Ca_3(AsO_4)_2$], as the most stable arsenate under alkaline, oxidized conditions, was likely the controlling solid phase in the FGD-amended soil. A decrease in soil pH by 1997 and likely sorption by soil oxyhydroxides and clay minerals at the lower pH resulted in less soluble As available for plant uptake and leaching.

ACCELERATED WEATHERING AND ARSENIC SPECIATION STUDIES

A laboratory and greenhouse study was begun in 2000 to determine the long-term bioavailability and leaching potential of As in CCP. The experiment consists of four components: 1) plant screening to assess the potential bio-availability of arsenic in CCP; 2) an accelerated weathering component designed to accelerate changes in the chemical speciation of arsenic in CCP that normally occur over many decades into an approximately 18-24 month time frame; 3) an assessment of the leaching potential and bioavailability of arsenic that will occur with time, i.e., before and after accelerated weathering is imposed; and 4) development of a model to predict the behavior of As in biosystems based on changes in chemical forms of arsenic, soil characteristics, soil As levels, and plant species.

The forms of As initially present in CCP or a soil-CCP mixture and the mineral phases controlling As solubility, as well as intermediate and end reaction products which may result from weathering, can be identified by use of appropriate analytical techniques, such as X-ray Diffraction (XRD) and selective sequential extraction. The rate at which alteration products of As appear would be largely dependent on environmental conditions and the original form of As in the soil. These conditions and the rate of weathering can be controlled in a laboratory or greenhouse setting. Cycles of wetting/drying, freezing/thawing heating/cooling and periodic temporary changes in pH are part of the accelerated weathering experimental protocol. Results to date indicate that As is being converted into more recalcitrant forms, although a periodic “pulse” of As in leachates has been observed.

CARBON SEQUESTRATION

TVA scientists are performing a DOE-funded research project addressing carbon sequestration using CCP as a sequestering medium for $CO_{2,}$, with subsequent conversion of CO_2 to an algal biomass for production of methane and other recyclable carbon-containing products. Three primary mechanisms likely control sequestration of CO_2 in the CCP:

1. Sorption (adsorption - specific and non-specific)
2. Anion-ligand exchange
3. Complexation and precipitation

Overcoming the mass transfer rate of CO_2 into solution makes the conversion of CO_2 to biomass difficult. A reactor has been developed that solves this problem and a recommendation has been submitted to DOE to seek a patent on the process. Process patentability is now under study by DOE. The end result of this project is to provide the basic data to develop a system that replaces 200 to 300 megawatts of fossil fuel CO_2 with recycled CO_2. The system could be deployed at most coal fired power facilities in the south and west. There is the potential of removing an aggregate of 10 to 20 megatons of carbon per year from fossil fuel generation using this technology.

SUMMARY AND FUTURE NEEDS

Use or disposal of CCP is becoming a much more environmentally sensitive issue. In the past, TVA researchers have focused on the benefits and environmental impacts of high-volume land application, practices to control environmental impacts of on-site storage, and on providing data that may affect current regulations or influence future legislation that governs off-site use or on-site storage of CCP. Regulatory issues regarding As and mercury (Hg) will drive future research for the near term. Since a reduction in the MCL (Maximum Contaminant Level) for arsenic to very low ppb levels is likely, research on innovative removal/treatment technologies for As in CCP and water will become a priority. Research is also needed in areas of Hg control technology at fossil plants, Hg stability in Hg control by-products, and removal/treatment technologies for Hg in water. TVA researchers are actively addressing these areas.

Acknowledgement

I gratefully thank Ms. Cheri Miller, TVA Fossil Power Group, Fuel Properties & By-Products, for contributing her extensive knowledge of coal combustion by-products, without which much of the progress in this area could not have been realized, and for her continued support of this research over the years.