

<Review>

재(석탄, 목재, 왕겨재)의 특성과 환경보호를 위하여 계분의 첨가 가능성에 관한 연구

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**Characteristics of Ash (Coal, Wood and Rice Hull) and Its Potential Use as an Additive in Poultry Manure for Protecting the Environment**

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**ABSTRACT** Ash amendment to manure holds potential as a method to neutralize manure for reducing odor and reduce phosphorus (P) solubility in runoff from fields where manure has been applied. This review focuses on the literature published about ash characteristics and their environmental uses. There is no uniform physico-chemical definition of the selected ashes (coal fly ash-CFA, wood ash-WA, and rice hull ash-RHA) used in various studies. These ashes vary greatly in their acidity (pH<6.0) or alkalinity (pH>12.5) based on the conditions at which they were formed and the composition of the ash source. CFA amendment to manure reduced manure-P solubility and application of CFA amended manure to agricultural soils is a method to improve water quality. WA may prove to be a valuable manure odor control amendment since WA contains a high level of carbon. A major biomass source is rice hull (husk) which provides an ash source (RHA). The rice hull and RHA are sources of silica, compromising about 20% and 60%, respectively. So far research has been directed at the use of CFA, WA and RHA as soil amendments, but there is potential use of these materials as manure additives to sequester P and reduce odors.

(Key words: Coal Fly Ash, Wood Ash, Rice Hull Ash, phosphorus solubility, acidity, alkalinity, odors, carbon, silica)

**Introduction**

Combustion of solid fuel always results in production of ash. Fossil fuel combustion residues, including fly ash, bottom ash, flue gas desulfurization (FGD) sludge, fluidized bed combustion fly ash (FBS), anthracite refuse fly ash (ANT), and oil ash, are disposed of in surface impoundments and land fills. Wood ash (WA) is a by-product of the wood industry resulting from burning of wood residues for either energy production or waste reduction. WA is different from coal ash, which has a lower alkalinity but higher silicon, aluminum, iron and heavy-metal content. In industry, rice hulls are burned to produce rice hull ash (RHA) as an energy source and to minimize the hull disposal problem. The potential of RHA for industrial application rely on the possibility of extracting the silica in a pure state.

Amorphous silica from RHA can be extracted using low temperature alkali extraction.

From a pollution-control stand-point, phosphorus, nitrogen, boron and the radioactive elements found in ash are particular importance to everybody. Further environmental problems come from air pollution, from possible radioactivity and related contaminants as well as from processes and technologies utilizing fly ash by-products (Ferraiolo et al., 1990). Environmental impact and effectiveness of waste-material use in agriculture are dominant topics in environmental policies of industrialized countries

Coal fly ash (CFA) is a mixture of iron and aluminum silicates, with lesser amounts of calcium, magnesium, potassium, sodium and sulfur oxides; the carbon content of the ash usually does not exceed 5%. CFA generally occurs as very fine spher-

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rical particles with an average diameter of  $\leq 10 \mu\text{m}$ . Up to 12 % of combusted fuel can become ashes in a normal coal combustion process (Hecht and Duvall, 1975). CFA ranges from extremely basic to acidic, usually in the range 6.5~11.0, and thus CFAs vary greatly in their neutralizing capacity depending on the source of the coal (Babcock, 1972). With the exception of acidic ash materials, CFA is effective in neutralizing acid soils (Adriano et al., 1980). Warren (1992) indicated that CFA has liming agent qualities; however, clay soils required nearly twice the amount of CFA to obtain the same unit increase in pH.

Wood ash (WA) is the inorganic and organic residues remaining after wood combustion. Tree type, soil composition, and climate cause variations in the WA content and chemical composition. Woods from temperate climates yield 0.1~1.0% ash, while tropical and subtropical woods yield up to 5%. Soft woods produce less ash than hardwoods. WA collected from combustion systems varies in physical and chemical properties depending on the temperature of combustion, the type of fuel, and where it is collected in the combustion system (Campbell, 1990). In addition, WA has a small particle size (averaging 230  $\mu\text{m}$ , Etiegni and Campbell, 1991) and low density (ranging from 0.52~0.88  $\text{g cm}^{-3}$ , Rosenfeld and Henry, 2000). Density varies according to the carbon content, with greater carbon contents resulting in lower density of the ash and lower concentrations of elements in the ash. In fluidized-bed combustion systems, the carbon content is 1%, while it is up to 70% in inefficient burners, with the typical range being 5~30% (Greene, 1988). WA contains the major and minor elements needed by trees for growth; calcium (7~33%), potassium (3~41%), magnesium (1~2%), phosphorus (0.3~1.41%), manganese (0.3~1.3 %) and sodium (0.2~0.5%) are the major elements. Essential trace elements zinc, boron, copper, molybdenum and other elements are provided by WA at parts per million levels, and concentrations of heavy metals are typically low. WA is substantially different in composition from coal ash, which is lower in pH but higher in silicon, aluminum, iron and heavy metal content (Campbell, 1990). WA is also used as a bulking and odor control agent in sludge-composting facilities (Logsdon, 1989; Hart, 1986). WA is a significant source of the nutrients P, K, Mg, Ca and lime (Naylor and Schmidt, 1986; Ohno and Erich, 1990). The neutralizing potential of WA typically ranges from 50 to 100% of that of limestone on a dry weight basis (Naylor and

Schmidt, 1986).

Burning rice hull as fuel to generate energy results in the waste product, RHA. Straw (wheat, barley, rape and other straw) is also used as fuel for combined heat and power production. Recycling of straw ash reduces the need for commercial fertilizer, counteracts the ongoing acidification and is a solution to the potential problem of disposing of ash resulting from future large-scale straw burning for energy production in some countries. However, biomass material such as RHA or other agricultural straw can be a potential and important energy source, and their biochemical properties may be useful for chemical industries (Chou and Chang, 1981; Stout, 1982). One of the major biomass components is the rice hull, which is produced in considerable quantities in several regions of the world. If not properly dealt with, rice hulls can have a negative impact on the environment in those regions (Amick, 1982; Basu et al., 1973). The rice hull and RHA are sources of silica comprising about 20% and over 60%, respectively. Silica has been widely used in vegetable oil refining, pharmaceutical products, detergents, adhesives, chromatograph column packing, and ceramics (Proctor et al., 1995). Asbestos consists of fibrous silicate minerals which can be used as thermal insulator. Silica is soluble under highly alkaline conditions ( $\text{pH} \geq 10$ ) and forms a rigid three-dimensional gel network when the pH of silicate solution is below 10 (Kalapathy et al., 2000a). After burning, the residual elements of RHA include plant nutrients such as P, K, Ca and Mg.

Essential micronutrients such as Cu and Zn can be toxic in excess, while heavy metals including Cd and Pb are highly toxic higher in the food chain (Tan, 1994). During combustion, N is almost totally lost. The composition of biofuel ash includes silicates, oxides, carbonates, sulfates, chlorides, and phosphates (Liem et al., 1983), and many of these compounds are water soluble.

Little information on the effects of CFA, WA or RHA on litter and/or manure microbial activity (odor) is available. Research on the use of CFA, WA or RHA for reducing soluble P in animal manure is relatively recent (Nahm, 2004). CFA ranges from extremely basic to acidic and thus varies greatly in its neutralizing capacity, depending in the source of coal (Babcock, 1972). In South Korea coal briquettes are popular for heating. After burning, CFA can be used as an additive for animal manure for protecting the environment (Yun, 2005). This paper

focuses the chemical and physical characteristics of CFA, WA and RHA, and their use for animal agriculture and for protecting the environment from pollution and utilization for animal agriculture.

### Phosphorus (P) and Its Effect on the Environment

Phosphorus is an important constituent of bone. Lack of sufficient dietary phosphorus results in poor mineralization of bone. Deficient chicks have soft, early bent bones that fracture readily. Marked deformity of the skeleton can be produced. P also is essential in energy metabolism, as a constituent of nucleic acids and for the activity of several enzyme systems (Card and Nesheim, 1972).

Concentrated poultry areas generally produce several times more manure P than is taken up and removed by crops in areas (Lander et al., 2000). The basic reason for the P imbalances is that large quantities of P are imported into those regions in feedstuffs. The surplus P has been building up in soils in concentrated poultry areas for several years, and there is increasing concern about P runoff from these high-P soils causing surface water quality problems (Sims et al., 1998).

### Coal Fly Ash (CFA)

#### 1. Physical and Chemical Characteristics of CFA

Part of the problem for use of CFA is that there is still no uniform physical-chemical definition of the selected fly ashes used in the various studies (Adriano et al., 1980; Roy et al., 1981). In most instances, fly and bottom ash from Kentucky and Illinois coals yielded leachates intermediate in elemental composition to leachates of Missouri and Wyoming coal ashes (Kopsick and Angino, 1981). CFA from a Missouri coal generated a leachate enriched in Pb, Zn, Cu, Fe, Mn, and Cd, reflective of the high Pb-Zn minerals present in the surrounding area (Table 1). With a pH of 3.0, this CFA has the greatest potential for groundwater contamination. Due to the high concentrations of Ca and Mg in most ashes of these studies, the majority of leachates are alkaline. With a pH of 3.0, this ash

**Table 1.** Trace elements found in coal fly ash (Liguria Region, 1998 quoted by Farraiolo et al., 1990)

Element	Concentration range (ppm)
Sb	0.5~8.4
As	5~5.6
Be	8.0~24
Cd	0.3~7.6
Hg	0.04~0.75
Pb	17~408
Cu	49~270
Se	1.4~13
Te	0.01~1
Tl	0.01~0.05
Cr	10~188
Ba	1000~1400
Ga	5.0~38
Mn	50~250
Mo	5.0~23
Ni	60~150
Sn	0.1~ 10
Sr	430~460
V	260~320
Zn	60~ 80
Zr	150~160

Method of Analysis for Coal Ash: A full spark source mass spectrometry analysis (SSMS) of the fly ash was used. (Fly ash production from coal is mostly imputable to coal-fed power stations, but the present amount of such production cannot be correctly assessed for lack of reliable data. Fly ash is mainly a result of the mineral compounds which are contained in the coal: a certain amount of unburned residue is also usually present within this particulate matter. Ash derived from combustion can be subdivided as follows: 1. Bottom ash 2. Fly ash. Fly ash is usually from flue gases through several systems such as gravity chambers, cyclones, multicyclones, wet scrubbers, electrofilters and fabric bag filters.)

is exceptionally acid. Conversely, leachates from Wyoming FA and bottom ashes exhibited low trace-metal concentration. Potential limitations of agronomic use of Australian CFAs include

low levels of N, excessive levels of B, high salt levels, their strongly alkaline pH values, high available water capabilities, and medium to high levels of plant-available Ca, Mg, and S (Aitken et al., 1984). Mattigod et al. (1990) and Eary et al. (1990) reported that major elements in fossil fuel waste disposal are Al, Ca, Fe, K, Mg, Na, Si and S, and minor elements in fossil fuel waste disposal are As, B, Ba, Cd, Cr, Cu, Pb, Mn, Hg, Mo, Ni, Se, V, and Zn. They said that CFA are extremely variable and are dependent on fuel composition and combustion processes. Trace elements were extracted from a coal-fired power plant electrostatic precipitator ash with nitric acid, hydrochloric acid, citric acid, redistilled water and ammonium hydroxide as extracts (Dreesen et al., 1977). They showed a positive correlation between those elements most extractable by water (B, F, Mo, and Se) or acid (As, B, Cd, F, Mo, and Se) and those elements most elevated in effluent waters (As, B, F, Mo, and Se). Seasonal variations in elemental concentrations show no strong general trends common to all sites (Alberts et al., 1985). They compared the concentrations of As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, and Zn as well as physico-chemical parameters for multiple sites in the basin/creek system and a pond without ash input from autumn to late summer. Chemical specification calculations indicate that most of the elements remain in the free hydrated or sulfate form throughout the study period.

Roy and Griffin (1982) reported that classification systems for CFA were developed to provide the basis of a uniform nomenclature that can be used by investigators in different disciplines to describe samples of CFA. Their system is based on chemical composition, pH, and particle size distribution. Seven taxonomic groups were generated by the distribution of three types of precipitation products of CFA: sialic ( $\text{SiO}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2$ ), ferric ( $\text{Fe}_2\text{O}_3 + \text{SO}_3$ ), and calcic ( $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ ). In this study, the seven basic units (groups) of classification system are based on chemical composition; they are formed by the intersections of three end members are the Sialic, Calcic, and Ferric groups.

Calcite formed through the dissolution of Ca from the ash and subsequent reaction with  $\text{CO}_2$  was absorbed by the initial alkaline leaching solutions. Iron, dissolved from the ash under acidic conditions, precipitated as amorphous coatings on CFA particles. Aluminum and Si dissolved from the glass of the ash was translocated and precipitated within alkaline environment as

an amorphous alumino silicate material best described as proto-imogolite.

The effect of CFA particle size, pH and  $\text{Ca}(\text{OH})_2$  presence on the solution and adsorption of boron by CFA in aqueous media has been studied (Hollis et al., 1988). Most of the soluble boron was found in the small ( $> 20 \mu\text{m}$  in diameter) particles of ash. Dissolution of boron was independent of the dissolution of Ca from CFA. Decreasing the pH from 12.5 to 6 increased both the solubility and the extractability of boron. Sorption of boron increased with increasing pH, up to 12. Chemical composition, total porosity and specific surface area of the solid adsorbent affected the absorptive capacity of CFA, but particle size distribution also must be taken into account (Peloso et al., 1983), since soluble boron was found in the small particles of CFA.

A concentration-particle size study has provided an experimental basis for testing current theories of trace element volatilization and condensation processes involved in coal combustion (Smith et al., 1979). There was generally good agreement in concentration of elements analyzed by more than one technique (Campbell et al., 1978).

Based on the concentration profiles, the elements can be divided into the distinct groups. One group consists primarily of the volatile element (e. g., As, Zn, and Se), whose concentrations decrease with increasing particle size. A second group, which demonstrated a minor or direct dependence on particle size, as in the case of Si, is apparently associated primarily with the CFA matrix. The last group of elements, which includes Ca, Sr, and the rare earths, showed small changes in their concentration profiles with a maximum in concentration in particles at approximately  $5 \mu\text{m}$ . Natusch et al. (1974) suggested that certain trace elements were volatilized in the furnace of coal-fired power plants and subsequently condensed on the surface of alumino-silicate particles as the fuel gases cool. Biermann and Ondov (1979) indicated that the thickness of the surface layer was small, even at particle sizes of  $0.1 \mu\text{m}$  where the surface layer was estimated to be about 20% of the particle diameter. The behavior of the relative concentrations of surface-enriched elements as a function of particle size was consistent with a slip-flow regime of aerosol mechanisms. Wadge et al. (1986) reported that both materials displayed an inverse relationship between particle size and extent of enrichment for

all the elements studied, but the degree of enrichment on the finest particles was lower than reported for CFA by other workers. They indicated that enrichment factors (EFs) for selenium were similar in both fly ash types (with EFs of 250 and 740). Despite the high crustal abundance (EF crust) values of certain elements in the two fly ash types, the same elements showed EF values of about unity when expressed with respect to the starting material.

Ramsden and Shibaoka (1982) related the optical and morphological properties of individual fly-ash particles to their compositions as determined by optical microscopy, scanning electron microscopy and electron microprobe analysis. Particle composition of a given CFA depends not only on the composition of the original mineral matter (which determines the bulk composition), but also on the history of each individual particle within the furnace, such as its residence time, maximum temperature, rate of cooling and to what extent it is recycled through reducing and/or oxidizing environments. They studied that whilst it is possible to use the combination of optical microscopy, scanning electron microscopy and electron microprobe analysis specifically to obtain information relating the optical and morphological properties of individual fly-ash particles to their compositions, such as analysis does not adequately characterize the ash as a whole.

The formation of deposits in coal-fired boilers is influenced by the physical characteristics of material arriving at the boiler tubes, so it is essential to understand the changes taking place when the particulate coal minerals are subjected to rapid heating in the flame. The work of Raask (1969) showed that the formation of ash spherulites in the furnace of a pulverized coal-fired boiler occurred when the viscosity of the material was in the range of  $10^3$  to  $10^5$  Ns/m<sup>2</sup>. Haynes et al. (1982) reported that CFA produced in high-temperature (1750°K) coal combustion has a bimodal size distribution with most of the mass occurring in the size range 1 to 20  $\mu$ m diameter. Most CFA is comprised of submicron particles (< 0.03  $\mu$ m), even though these constitute 1% of the total mass. Both kinds of particles are coated with a surface deposit of volatile trace elements such as As, Sb and S.

Caruccio and Geidel (1978) suggested that the addition of an alkaline CFA would raise the pH of the acidic coal refuse, lower its hydraulic conductivity, and lower the rates of gas

exchange in the refuse, all of which would presumably limit acid mine drainage production. Stewart et al. (1997) reported that both the 20 and 30% treatments of alkaline CFA were very effective; however, the decline in pH of one of the 20% columns indicated that the pyrite in that column was not permanently neutralized. Alkaline CFA at high bulk blending rates ( $\geq 20\%$ ) appears to be an effective long term control of acid mine drainage, with only boron (B) and  $\text{SO}_3^{2-}$  appearing to leach at any significant levels.

Alkaline CFA contains a number of identifiable phases that account for leachate characteristics during weathering (Warren and Dudas, 1984). The initial stages of weathering, characterized by the release of high concentrations of Ca, Na, and K and extreme solution alkalinity is related to the hydrolysis of CaO flecks and dissolution of highly soluble surface salts. More of the total Na than the total K was associated with soluble salts on the surface of ash particles. Hydrolysis of CaO and subsequent dissolution of  $\text{Ca}(\text{OH})_2$  was responsible for the extreme alkalinity (> 12) of the initial leachates (Warren and Dudas, 1984). Release of certain elements such as B, As, or heavy metals such as Zn, Cd, Cr, and Pb may result in contamination of ground and surface waters and soils. Dissolution of large quantities of soluble salts or generation of extreme alkalinity in the case of majority of CFA may also result in problems (Warren and Dudas, 1984). In spite of the variabilities involved, pH alterations in solution and trace metal association with amorphous oxide sinks were found to yield a measure of consistency among all the CFA studied (Theis and Wirth, 1977).

## 2. Reducing Animal Manure-P Solubility with CFA and P Bioavailability after Ashing Poultry Litter

Odors from broiler production facilities are the consequence of odorant molecules produced by microbial activity in the litter including ammonia (Lacey et al., 2004). Depending on the composition of the parent coal, combustion conditions and final handling, CFA may vary widely in pH, salt and metal content (Adriano et al., 1980). Consequently the chemical properties of ash may have a significant impact on microbial activity and litter chemistry.

The release of soluble P to runoff in high P soil where P loss in runoff is a concern can be reduced by several coal combus-

tion by-products (Stout et al., 1998). Al rich amendments such as aluminum sulfate or aluminum chloride provide a means for reducing P-solubility in animal manure and the risk of offsite P movement from uncovered manure storage areas and application of stockpiled or composted manure (Choi, 2004). Reduced soluble P concentrations in treated manure would bring N and P nutrient ratios more in balance with the nutritional needs of plants than the untreated material when land-applied. Removal of P from municipal waste waters and lake waters as a contaminant has been achieved by adding high pH, high Ca coal-combustion wastes (Vinyard and Bates, 1979). A major mechanism for P removal from wastes is P precipitation by Ca, which makes the Ca content of coal combustion ash an important parameter. High pH (above 10) and high soluble Ca contents of ash materials enable P removal rates up to 30 (mg  $\text{PO}_4\text{-P}$ ) (g CFA)<sup>-1</sup> within a 3 hour period of time (Vinyard and Bates, 1979). Gray and Paulschwab (1993) reported that the combustion of high pH and readily available Ca in the bottom ash and bottom/CFA mixture favored rapid precipitation of calcium phosphates. However, chemical limitations of raw ash materials include toxicity induced by high alkalinity, high salinity, and plant nutritional deficiencies induced by high pH (Mulhern et al., 1989).

Dao (1999) found that caliche (a natural source of Ca found in the calcic layer of soil in semiarid and arid regions), alum, and CFA (class C coal combustion ash) reduced water-extractable P (WP) in stockpiled cattle manure by 21, 60, and 85% and by 50, 83, and 93% in composted manure when applied at the 0.10 kg kg<sup>-1</sup>. Dao (1999) studied the effects of alum, caliche, and CFA (coal fly ash) on WP (water soluble P) concentrations in stockpiled and composted cattle manure at rates of 0, 0.10, 0.29, and 0.50 kg kg<sup>-1</sup> manure. Dao and Daniel (2002) reported that CFA reduced solution-phase dissolved reactive phosphorus (DRP) at all rates  $\geq 1$  g L<sup>-1</sup> by 52 and 71% in total suspended solid (TSS30) and TSS100 (100 gL<sup>-1</sup> total suspended solids), respectively. Dou et al. (2003) reported that fluidized bed combustion fly ash (FBC) reduced readily soluble P by 50 to 60% at a rate of 400 g kg<sup>-1</sup> for all three manures (dairy, swine or broiler litter manure). Flue gas desulfurization by-product (FGD) reduced readily soluble P by nearly 80% when added to swine manure and broiler litter at 150 and 250 g kg<sup>-1</sup>. In all cases, reduction in readily WP is primarily associated with

inorganic P with little change in organic P {Total phosphorus (Pt) - inorganic phosphorus (Pi) in this study}.

Vincini et al. (1994) reported that alkaline CFA did not inhibit microbial activity and respiration in 10% - or 20% - amended swine manure. The reduction in CO<sub>2</sub> production of the amended manure is probably due to the high pH values of the manure caused by CFA addition, rather than to an inhibition of microbial activity. A marked mobilization of inorganic P compounds of CFA, effective at enriching the fertilizer value of swine manure, occurred in the amended manure, possibly as a consequence of the microbial activity. This P mobilization was accompanied by an appreciable dissolution of Mn and B, the litter being so marked in the 20% CFA-amended manure that a careful consideration of B soil content and sensitivity of crops should be required before incorporation of the material into soil. Vincini et al. (1994) used 1,500 mL of swine manure as a control or 1,500 mL of swine manure and 150 g of CFA (CFA/manure ratio of 10% w/v) or 1,500 mL of swine manure and 300 g of CFA (20% w/v). There was another general trend of decreasing WP with increasing treatment rates of alum or coal combustion by-products for all three manures (dairy, swine and broiler). Results from a study (Toth et al., 2001b) suggested that the most environmentally sensitive P fractions (soluble P) in animal manures can be significantly reduced by treating the manure with chemical amendments, including several types of coal-combustion by-products. Amendment effects are likely due to a combination of complexation of P with metal ions and pH changes. Differences in amendment effects between the dairy and swine samples should be investigated further.

It is relevant whether the residual ash following the burning of poultry litter would have value as a source of nutrients. Four samples of turkey litter ash residue have been evaluated for phosphorus bioavailability utilizing a turkey growth assay with bone ash as the response criterion (Akpe et al., 1984). Availabilities obtained were 81, 88, 78 and 72% in comparison to availability from calcium phosphate monobasic monohydrate at 100%. Akpe et al. (1984) concluded that this material showed promise as a source of phosphorus in poultry nutrition. The phosphorus biopotency from litter ash for broiler chicks, determined from 3-wk body weight data (Muir et al., 1990), was estimated to be 79.1 and 82.9% of the standard in two separate experiments. Both estimates obtained in Experiment 2 were sig-

nificantly different from the dicalcium phosphate standard.

### 3. Organic Waste with CFA Used for Soil Application

CFA alone is not an adequate source of the macronutrients N and P (Carlson and Adriano, 1993). During coal combustion, N is volatilized and CFA-P is relatively unavailable (Bradshaw and Chadwick, 1980). In contrast, organic wastes tend to be imbalanced sources of N and P nutrients for plants. For poultry manure, approximate N:P:K ratios are 2.5 : 10 : 0.9 (Edwards and Daniel, 1992). When poultry manures are used to supply total crop N requirement, P will be in excess for most field and forage crops. Jackson et al. (1999) suggested that for the combined applications of organic wastes and CFA, the use of an organic waste could alleviate the deficiency of macronutrients in CFA, while CFA can act as a bulking agent for the organic wastes. Such a combination could substantially reduce odor. In one study, Jackson et al. (1999) applied mixtures of CFA with either poultry litter (PL) or sewage sludge (SS) to field plots at rates 100 and 120 Mg ha<sup>-1</sup> for CFA/PL and CFA/SS, respectively. Combinations were mixed prior to application with a small rotary hoe at the dry weight ratio of 4:1 and 2:1 for CFA/PL and CFA/SS, respectively. Leaf tissue data confirmed an increase in available As from the CFA/PL mixtures, while leaf tissue Se was more dependent on the total Se concentration of the ash. Schumann and Summer (1999) reported that yield improvement of maize grown with mixtures of CFA with sewage sludge or poultry manure ranged from 30 to 49% and 30 to 71%, respectively. Organic materials applied alone achieved only 54 and 62% of the maximum potential, while growth of maize on poultry manure and CFA mixtures was 94 % of the best performing fertilized treatment. P and K were the main nutrient deficiencies, while B phytotoxicity and an imbalance in the P:K:Mg ratio were causes of plant growth reduction.

### 4. Effects of CFA Application to Agricultural Soils and Surface Water Quality

High rates of fertilizer and manure application in some countries of the world have resulted in the majority of agricultural soils having excessive levels of plant-available P in comparison to crop needs (Sharpley et al., 1998). High levels of P in soils are an environmental concern rather than an agronomic one,

since runoff from soils containing elevated levels of P contributes to eutrophication of receiving fresh water (Carpenter et al., 1998). An important component of the P export is the dissolved P that is available to algae. Its loss by surface runoff can be reduced by lowering its solubility in heavily manured and fertilized soils. This may be effectively accomplished under certain conditions by applying coal combustion by-products (CCBs) to critical source areas (Stout et al., 1999).

More attention is being placed on controlling runoff from agriculture and other nonpoint sources of pollution as significant water quality issues remain unsolved. One major unresolved problem is the accelerated or cultural eutrophication of surface waters resulting from nutrient inputs that stimulates algal and aquatic plant growth (Thomann and Mueller, 1987). Surface-water use for aesthetics, fisheries, recreation, industry and drinking is affected by this eutrophication and thus results in serious local and regional economic impacts. Much of this concern has focused on P, even though N and C are required for algal growth as well. This is due to difficulties in controlling the air-water exchange of N and C, and the fixation of atmospheric N<sub>2</sub> by blue-green algae, which often results in P being the nutrient that promotes accelerated eutrophication (Sharpley et al., 1994).

A sound P management program is essential for profitable crop production and environmental conservation (Sharpley et al., 1994). Judicious fertilizer use can increase vegetative cover resulting in reduced erosion and runoff potential; nonpoint sources of P on agricultural runoff now contribute a greater portion of freshwater inputs, due to easier identification and recent control of point sources (Sharpley et al., 1994). Although P management is an integral part of profitable agri-systems, continued inputs of fertilizer and manure P in excess of crop requirements have led to a build-up of soil P levels, particularly in areas of intensive crop and livestock production.

Coal-combustion by-products have long been introduced into agricultural systems to improve soil physical properties and crop yield, but a recent focus is that of sequestering P. Stout et al. (1999) reported that converting water-soluble phosphorus to less soluble forms with lime or calcium-containing coal combustion by-products can reduce the release of soil phosphorus to surface runoff. Baligar et al. (1997) found out that CCBs and phosphate rock (PR) application increased plant P content and dry matter yield of shoots and roots by improving soil Ca availability and

reducing Al toxicity. They suggested that this improved plant response was likely related to alleviation of Al toxicity by  $\text{CaCO}_3$  contained in the BP. In addition to raising the pH to an acceptable level for plant growth, the dolomitic lime supplied needed Mg for plants, thereby maintaining a good balance between available Ca and Mg for plants in the CCB- and PR-amended soils.

Two CCBs, FBC and FGD, have been shown in recent studies to reduce the solubility of soil P without decreasing the plant-available P appreciably (Stout et al., 1998). When applied to soil, the  $\text{Ca}^{2+}$  and  $\text{OH}^-$  in CCBs convert the P into less soluble P fractions. Dissolved P export overall could be substantially reduced by application of CCBs to critical P source areas on a water shed (Stout et al., 1999). Stout et al. (2000) reported that on grassed soils, FBC, FGD and agricultural gypsum (GYP) reduced DP concentration in runoff by 20, 43 and 33%, respectively, but did not affect As, Cd, or Pb concentrations in runoff. Also on grassed soils, the high application rate of FGD reduced total phosphorus (TP) in runoff by 35%. Application of CCBs to high P soils in zones of high surface runoff potential, has the potential to reduce P export without affecting crop production.

Sharpley et al. (2001) evaluated the P index on sites ranging in soil type, topography, and nutrient management. Mehlich-3 soil P concentration accounted for 86% of the variation in dissolved P concentration in surface runoff from sites that had not received P in the previous six months, but was not related to surface runoff P from recently manured sites. Using a P index, which considers transport and source effects on P loss potential, nearly 80% of the variability in surface runoff P concentration and loss was accounted for in both unmanured and manured sites. Transport factors included erosion, surface runoff and subsurface flow and whether the field was connected and flow contributed to discharges into the stream; source factors included soil test P concentration and the form, rate, method and timing of applied P (Lemunyon and Gilbert, 1993; Gburek et al., 2000). Fields were designated as highly vulnerable to P loss when there was high P availability due to soil test P concentrations and/or P application in fertilizer or manure coincided with high surface runoff or potential of erosion. In cases where subsurface P transport is important, another factor to consider is preferential flow through soil macropores (Leytem et al.,

1999). The P index was not developed originally to quantitatively predict P loss from a watershed, but it was developed to serve as a qualitative assessment tool to rank site vulnerability to P loss, helping to identify and prioritize management options for P. The P index ultimately serves as an educational tool that facilitates interactions between planners and farmers, helping to determine the water quality impacts of management decisions (Sharpley et al., 2001).

The P in CFA may not be readily available for plant growth and, thus addition of CFA to soils may decrease the availability of fertilizer P (Adriano et al., 1978; Carlson and Adriano, 1993). Martens (1971) suggested that increases in soil pH caused by the addition of CFA could explain the reduced availability of P to corn, relative to monocalcium phosphate. O'Reilly and Sims (1995) examined the effects of amending an Evesboro loamy sand with CFA (0~30%, w/w) on P availability and adsorption-desorption. CFA increased soil test P from 13  $\text{mg kg}^{-1}$  to 34  $\text{mg kg}^{-1}$  but had little effect on readily desorbed P. The adsorption or desorption of P was not markedly influenced by CFA in either batch or incubation studies except at the highest CFA and P rates. In the batch study, the greatest increases in P adsorption were seen at the 20% and 30% CFA rates and P equilibrium concentrations  $\geq 20 \text{ mg L}^{-1}$ .

The amount of base obtained from CFA through direct reaction with acids is much greater than that obtained from dissolution in pure water, a significant of the chemical utilization of CFA (Green and Manahan, 1978). CFA dissolves in discrete steps with increasing acidity, thereby indicating the presence of specific fractions within the material. Determination of total available base in CFA can be accomplished via dissolution in dilute mineral acid, followed by either back-titration with NaOH, or determination of dissolved sulfate, Na, K, Ca, and Mg (Green and Manahan, 1978). However, the most significant problem is that there may be considerable variation in the composition of coal ashes, and thus total available base, from different power plants, even in separate samples of ash from the same generating plant (El-Mogazi et al., 1988).

## Wood Ash (WA)

### 1. General Characteristics of WA



WA is the remaining inorganic and organic residue from combustion of wood. Tree species, soil type, and climate affect the ash content and chemical composition. The physical and chemical properties of WA collected from combustion systems vary greatly depending on the combustion temperature, the type of fuel (species of wood and amount of bark), and where the WA is collected in the combustion system (Campbell, 1990). In a study of WA and its properties, Etiegni and Campbell (1991) found that as combustion temperature increased from 538 to 1093°C, WA yield decreased approximately 45%. There were decreases in potassium, sodium, zinc, and carbonate contents with increased temperature, while other metal ions remained constant or decreased. WA leachate contained 92% hydroxide and 8% carbonate, and as the pH of WA decreased from 13 to 5, total dissolved solids increased by 500%. The average particle size of the ash was 230  $\mu\text{m}$ . There were large porous carbon particles and inorganic particles which reacted with water to form rosette clusters seen by scanning electron micrographs (Etiegni and Campbell, 1991).

The predominant elements of WA have been reported to be Ca, Mg, and K, while the major constituents of bark boiler ash are Ca, Al, Si, K, Mg, and N (Someshwar, 1996) (Table 2). WA is composed of the major and minor elements needed for tree growth. Major elements include Ca (7~33%), K (3~4%), Mg (1~2%), P (0.3~1.4%), Mn (0.3~1.3%), and Na (0.2~0.5%). Trace minerals essential for plant growth include Zn, B, Cu, Mo and others at parts per million. There are typically low levels of heavy metals, and the total metal concentration in the ash is quite different from the extractable or available concentration. The composition of WA is also quite different from CFA, as CFA has a lower alkalinity but higher silicon, aluminum, iron, and heavy metal content (Campbell, 1990; Etiegni, 1990; Greene, 1988). Sander and Andren (1997) reported that combustion of wheat, barley, and rye straw at a Swedish power plant produced an ash with the major constituents of K, Ca, and Mg. These reports suggest that alkali metals and alkaline earth metals are predominant in ashes formed from the combustion of wood (Someshwar, 1996) and other plant biomass. These compounds impart a high pH to WA and make it appropriate as a liming agent to increase the pH of acid soils.

In WA, the alkaline metal and earth elements are present mainly in the form of oxides, hydroxides, and carbonates such

as potassium oxide, calcium oxide, potassium carbonate, and calcium carbonate (Campbell, 1990; Khanna et al., 1994). Over time, the oxides react exothermically with moisture and carbon dioxide to form hydroxides and carbonates. A highly alkaline ash is produced from these compounds with a typical pH in the range of 11 to 13. The less soluble calcium hydroxide and calcium carbonate react slowly with acids, while the soluble potassium carbonate and potassium hydroxide react rapidly (Campbell, 1990; Khanna et al., 1994; Rowell, 1988).

The capacity for ash to neutralize is often defined by its

**Table 2.** Elemental composition of wood ash (Tulonen et al., 2002)

Element	Concentration (g kg <sup>-1</sup> )
P	6.1
K	12.8
Ca	248
Mg	10.4
Mn	4.8
S	8.4
Na	5.3
Fe	5.5
Al	11.4
Zn	1.2
Cu	0.11
Pb	0.01
Cr	0.03
Cd	0.007

Method of Analysis for Wood Ash: For chemical analysis, subsamples were collected from the experimental tanks immediately after mixing of water, one hour after ash addition, and every second day from then on. Water temperature and pH were measured daily. Analysis for PO<sub>4</sub>-P, total P, NO<sub>2</sub> + NO<sub>3</sub>-N, and total N were performed with standardized methods using an Akea autoanalyzer (Lachat [Milwaukee, WI] QC 8000). All elemental concentrations (atomic absorption spectrometer [AA] analyzer, Varian [Palo Alto, CA] Spectra AA 220 Fast Sequential) and concentrations of SO<sub>4</sub><sup>2-</sup> (Dionex [Sunnyvale, CA] 2000i ion chromatograph) were determined at the beginning and end of each experiment. All analyses were performed in the laboratory at Lammi Biological Station.

calcium carbonate equivalent, which is highly variable (Campbell, 1990; Etiegni and Campbell, 1991; Naylor and Schmidt, 1986). The increase in soil pH to which ash or lime has been applied results from this neutralizing capacity and from soil chemical and physical properties such as exchangeable Al, cation exchange capacity, base saturation, texture, and organic matter content. All of these factors contribute to a soil's capacity to buffer against pH changes (Khanna et al., 1994; Rowell, 1988).

## 2. Reducing Odors with WA

Using WA as a biosolids compost amendment has a significant advantage in that it has an ability to reduce odors during the composting process and the finished product. Much of the carbon found in WA, especially materials that do not achieve complete combustion from boilers, exists in a form similar to that found in activated carbon (C) filters. This carbon form has an extremely high surface area to volume ratio, so it is very efficient at adsorbing volatile organic produced during composting. Activated carbon filters efficiently remove organic sulfur-containing compounds such as dimethyl disulfide (DMDS) and methyl mercaptan, which are responsible for many of the nuisance odors generated during biosolids composting (Carpenter and Beecher, 1997).

Compounds identified as odors emitted from biosolids following application to forest soil included DMDS, dimethyl sulfide (DMS), carbon disulfide (CS<sub>2</sub>), ammonia (NH<sub>3</sub>), trimethyl amine (TMA), methyl ketone, and acetone (Rosenfeld, 1999). Banwart and Bremmer (1975) reported that 55 to 98% of the total S evolved from biosolids application to soil in aerobic conditions was DMDS. When emissions from chicken, cattle, horse, and swine manure were analyzed, the NH<sub>3</sub>-N flux was found to account for 99.3% of the N flux while amines accounted for 0.7% of the N flux; TMA emissions exceeded the sum of the other amines by three times (Schade and Crutzen, 1995).

Rosenfeld and Henry (2000) reported that odor unit emissions were positively correlated with DMDS emissions. To control biosolids odor, WA containing 87, 32, 27, 5.4, or 0.24% carbon was incorporated with biosolids (1 : 1 dry weight ratio). The WA possessed surface areas of 520, 85, 72, 25, and 2.1 m<sup>2</sup> g<sup>-1</sup>, respectively. Ash addition reduced odor unit (the converted values of dilution-to-threshold values) and emissions of DMDS,

DMS, and CS<sub>2</sub> when compared with the biosolids control, depending upon ash C content and surface area. Although ash additions reduced emissions of acetone, TMA and NH<sub>3</sub> reduction was not consistently significant.

## Rice Hull Ash (RHA) and Its Application

Serious environmental pollution problems can be caused by the production of solid wastes from biomass materials, including agricultural residues, animal manure and forests. Many scientists consider biomass to be a potential and important energy source (Raman et al., 1980; Stout, 1982). One of the major biomass sources is rice hull (husk), which is produced in large quantities in several areas of the world.

Research directions into the use of RHA have been much different from those of CFA and WA. The main components of rice hull are cellulose, hemicellulose, lignin, and silica (Juliano, 1985; Juliano et al., 1987). Rice hull (RH) and RHA are sources of silica, comprising about 20% and over 60% respectively (Table 3). RH has now become a source for a number of silicon compounds, including silicon carbide, silica, silicon nitride, silicon tetrachloride, zeolite, and pure silicon (Sun and Gong, 2001). Silica has been utilized for vegetable oil refining, pharmaceutical products, detergents, adhesives, chromatograph column packing, and ceramics (Proctor et al., 1995). Asbestos is fibrous silicate minerals used as thermal insulation. Silica dissolves in highly alkaline conditions (pH ≥ 10) and when the pH of silicate solution is lowered below 10, a rigid three-dimensional gel network forms (Iler, 1979; Kamath and Proctor, 1998).

Combustion of RH with and without coal in the presence of a pilot flame in a modified fluidized bed was investigated by Luan and Chou (1990). Addition of coal to RH resulted in a much smoother temperature distribution of the reactor and the agglomerating phenomena disappeared. The addition of coal also increased the bulk temperature and changed the composition, the particle size distribution, and the specific surface area of RHA. Content of RHA was insensitive to the addition of coal to the solid feed when the coal fraction in the solid feed was less than 30%.

A rapid, simple, and low-energy method has been developed to produce silica gel from RHA by alkali solubilization and

**Table 3.** Analysis of Rice Hull Ash (RHA) (Sun and Gong, 2001)

Component	Content (%)
SiO <sub>2</sub>	86.9 ~97.3
K <sub>2</sub> O	0.58 ~ 2.5
Na <sub>2</sub> O	0.0 ~ 1.75
CaO	0.2 ~ 1.5
MgO	0.12 ~ 1.96
Fe <sub>2</sub> O <sub>3</sub>	trace ~ 0.54
P <sub>2</sub> O <sub>6</sub>	0.2 ~ 2.85
Cl	trace ~ 0.42

Method of Analysis for Rice Hull Ash: Silica was extracted using 1M NaOH. The procedure involved boiling RHA (100 g) in 1 M NaOH (500 cm<sup>3</sup>) for 1 h to produce sodium silicate followed by filtering the solution through Whatman No. 41 filter paper to separate the carbon residue. The volume of this silicate solution was reduced to 250 cm<sup>3</sup> by boiling. Silica concentration in the concentrated silica extract was used by appropriate dilution. Measured volumes of silicate solutions containing 6.6 g of silica were placed into 250 cm<sup>3</sup> plastic beakers (Kalapathy et al., 2000a).

subsequent acid treatment (Kamath and Proctor, 1998). According to these findings, the novel silica gel which has a moisture content of  $\geq 65\%$  has certain physical and chemical properties that are similar to Trisyl 300, a commercial silica gel. Kalapathy et al. (2000a) reported that the silica gels produced were heated to 80°C for 12 hr to obtain xerogels. Silica and mineral contents of xerogels were determined by energy dispersive X-ray (EDX) and inductively-coupled plasma (ICP) emission spectrometers, respectively. Xerogels produced from RHA at an extraction yield of 91% were Na, K, and Ca. Acid washing prior to extraction resulted in silica with a lower concentration of Ca ( $\leq 200$  ppm). In another study, Kalapathy et al. (2000b) suggested that gelation pH and silica concentration of gel-forming solution had significant effects on the density and the mechanical strength of xerogels produced from rice hull silica. However, Kalapathy et al. (2002) indicated that silica xerogels produced by the improved using citric and oxalic acid had sodium content of 0.52% and 0.22%, respectively. Moreover, silica, sodium, carbon, and oxygen content of silica xerogels varied depending on the pH and the type of acid used for the

production of these xerogels.

The mineral ash content of straw includes plant nutrients such as P, K, Ca, and Mg. Other minerals such as Cu and Zn are essential micronutrients which can be toxic in excess, while heavy metals such as Cd and Pb are toxic higher in the food chain (Tan, 1994). During combustion, N is almost totally lost during combustion. Silicates, oxides, carbonates, sulfates, chlorides, and phosphorus are found in biofuel ash (Liem et al., 1983), and many of these are water soluble. The ash from straw is strongly alkaline and has a liming effect and it also contains organic compounds and chemical from incomplete combustion (Axenbom et al., 1991). The composition of 79 samples of straw ash from seven heating plants in Sweden was analyzed with the aim of evaluating straw ash as fertilizer and liming agent (Sander and Andren, 1997). The variation in straw ash composition was explained mainly by ash fraction (bottom straw ash vs. fly straw ash) and straw type (wheat, barley, rye, rape) but also by burning loose straw or rope. Compared with concentration of Zn, Pb, and Cd in bottom ash, levels in fly ash were 10~90 times higher. Straw fly ash also contained more Cu and K compared with bottom ash. The Cd:P ratio was 0.03 in bottom ash and 0.6 g Cd:P kg in fly ash. Ash from rape straw had a higher Ca content and liming effect compared with ash from cereal straw; e.g., the liming effect of rape ash was more than three times higher than that of wheat ash. The liming effect varied between 3.5 and 44% CaO and depended mainly the Ca content. The average P content was 1.7% (0.2~44%), with slightly higher concentration in rape ash than in wheat ash.

## Future Research

This study focused on the use of ashes in animal agriculture. Up until now, not a significant amount of research has been done on the use of ashes as livestock manure additives. As indicated previously in this article, CFA, WA and RHA all have pH neutralizing capabilities. Their potential ability to control the pH of manure (litter) makes them a useful additive since they help to inhibit microbial growth and consequently odor. Research studies have shown that ashes have the potential to be used to reduce the solubility of P in manure and therefore reduce the amount of soluble P runoff into surface and ground

waters. Further research into these topics is promising for the use of ashes as manure additives. In South Korea, coal briquettes (CB) are a popular heating source which produce a large amount of ash. Utilization of this ash to control odor and P content of manure holds promise in the future but no research into this ash source has been done so far in South Korea.

## 적 요

재는 가축분을 중성화 시키며 토양에 산포하면 악취를 저감시키는 역할을 하며 하천에서 P의 양을 감소시킬 수 있다. 그러므로 본 연구에서는 재의 특성과 이들의 첨가가 가져올 환경적인 이용에 관해서 언급하였다. 재는 아직도 물리적·화학적으로 일정한 정의가 없다 (석탄재-CFA, 목재재-WA, 왕겨재-RHA). 이들 재를 형성하고 있는 조건과 조성에 따라 산도는 6.0이하 그리고 12.5이상까지 이른다. CFA를 분중에 첨가하면 분중에 녹아있는 P의 양이 감소되어 토양에 산포하면 수질을 향상시킨다. WA는 WA 자체에 많은 탄소 원자를 갖고 있기 때문에 분에서 발생하는 냄새를 제거할 수 있다. RHA는 재중에 20~60% 가량이 실리카이다. 현재까지 CFA, WA 그리고 RHA를 토양에 산포하여 미치는 영향에 대한 연구는 많이 되어 있으므로 앞으로 가축분에 첨가하면 분중의 P과 악취를 낮출수 있는 연구가 필요하다.

(색인어 : 석탄재, 목재재, 왕겨재, 인의 분해도, 산도, 알카리도, 냄새, 탄소, 실리카)

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## References

- Adriano DC, Page AL, Elsewli AA, Chang AC, Straughan J 1980 Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review. *J Environ Qual* 9: 338-344.
- Adriano DC, Woodford TA, Ciravolo TG 1978 Growth and elemental composition of corn and bean seedlings as influenced by soil application of coal ash. *J Environ Qual* 7:416-423.
- Aitken RL, Campbell DJ, Bell LC 1984 Properties of Australian fly ashes relevant to their agronomic utilization. *Aust J Soil Res* 22:443-450.
- Akpe MP, Waibel PE, Morey RV 1984 Bioavailability of phosphorus in poultry litter biomass ash residues for turkeys. *Poul Sci* 63:2100-2107.
- Alberts JI, Newman MC, Evans DW 1985 Seasonal variations of trace elements in dissolved and suspended loads for coal ash ponds and effluents. *Water Air Soil* 26:111-120.
- Amick JA 1982 Purification of rice hull as a source of solar grade silicon for solar cells. *J Electrochem Soc* 129:864-871.
- Axenbom A, Kristensen O, Praks O 1991 Halm Some Bransle for Framtide Elproduktion-Em Sammanfattening av Dagslaget (In Swedish with English summary), Vattenfall, 16287 Vallingby, Swine p. 84-95.
- Babcock A 1972 Spoil, gob, and fly-ash produce plant supporting soils. *Nat Ash Assoc Tech Bull No.* 12.
- Baligar V, He ZL, Martens DC, Ritchey KD, Kemper WD 1997 Effect of phosphate rock, coal combustion by-product, lime, and cellulose on ryegrass in an acidic soil. *Plant Soil* 195: 129-136.
- Banwart WL, Bremmer JM 1975 Formation of volatile sulfur compounds by microbial decomposition of sulfur-containing amino acids in soils. *Biol Biochem* 7:359-367.
- Basu PK, Kung CJ, Lynn S 1973 Manufacture of silicon tetrachloride from rice hulls. *AICHEJ* 19:439-442.
- Biermann AH, Ondov JM 1979 Applications of surface-deposition models to size-fractionated coal fly ash. *Atmosph Environ* 14:289-299.
- Bradshaw AD, Chadwick MJ 1980 *The Restoration of Land.* Univ. of California Press, Berkeley, Cal., USA.
- Brady NC 1974 *The Nature and Properties of Soil.* 8<sup>th</sup> Ed., MacMillan Publishing Co., New York, USA.
- Campbell AG 1990 Recycling and disposing of wood ash. *Tappi J* 73:141-148.
- Campbell JA, Lau JC, Nielson KK, Smith RD 1978 Separation and chemical characterization of fine-sized fly-ash particles. *Analytical Chem* 50:1032.
- Card LE, Nesheim MC 1972 *Poultry Production.* Lea & Febiger Pub. Co., Philadelphia, Pa, USA pp. 198-199.
- Carlson LC, Adriano DC 1993 Environmental impacts of coal

- combustion residues. *J Environ Qual* 22:227-234.
- Carpenter A, Beecher N 1997 Wood ash finds niche in bio-solids composting. *Biocycle* 38:37-44.
- Carpenter SR, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VF 1998 Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol Applic* 8:559-562.
- Caruccio FT, Geidel G 1978 Geochemical factors affecting coal mine drainage Quality, In *Reclamation of Drastically Disturbed Lands*, eds Schaller, F.W. and Sutton, P. ASA, CSSA, and SSSA, Madison, WI, USA, p. 129-137.
- Choi IH 2004 A study on reducing the environmental pollutants from animal feces and urine. Ph.D. Thesis, Taegu University, Gyong San, South Korea, June.
- Chou TC, Chang KT 1981 Gasification of baggage in the presence of a pilot flame in a modified fluidized bed. *Ind Eng Chem Process Des Dev* 20:161-183.
- Dao TH 1999 Coamendments to modify phosphorus extractability and nitrogen/phosphorus ratio in feedlot manure and composted manure. *J Environ Qual* 28:1114-1119.
- Dao TH, Daniel TC 2002 Particulate and dissolved phosphorus chemical separation and phosphorus release from treated dairy manure. *J Environ Qual* 31:1388-1396.
- Dou Z, Zhang GY, Stout WL, Toth JR, Ferguson JD 2003 Efficacy of alum and coal combustion by-products in stabilizing manure phosphorus. *J Environ Qual* 32:1490-1498.
- Dreesen DR, Gladney ES, Owens JW, Perkins BL, Wienke CL 1977 Comparison of levels of trace elements extracts from fly ash and levels found in effluents waters from a coal-fired power plant. *Environ Sci Tech* 11:1017-1021.
- Early LE, Rai D, Mattigod SV, Ainsworth CC 1990 Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residue: II. Review of the minor elements. *J Environ Qual* 19:202-210.
- Edwards DR, Daniel TC 1992 Potential runoff quality effects of poultry manure slurry applied to fescue plots. *Trans ASAE* 35:1827-1834.
- El-Mogazi O, Lisk DJ, Weinstein LH 1988 A review of physical, chemical, and biological properties of fly ash and effect on agricultural ecosystems. *Sci Total Environ* 74:1-12.
- Etiegni L 1990 Wood ash as a soil additive and liming agent. Ph.D. Dissertation, Forest Products Department, Univ of Idaho. Moscow, Idaho. USA.
- Etiegni L, Campbell AG 1991 Physical and chemical characteristics of wood Ash. *Biores Technol* 37:173-177.
- Ferraiolo G, Zilli M, Converti A 1990 Fly ash disposal and utilization. *J Chem Tech Biotechnol* 47:281-289.
- Furr AK, Parkinson TF, Heffron CL, Reid JT, Haschek WM, Gutenmann WH, Bache CA, St. John LE, Jr., Lisk DJ 1978 Elemental content of tissues and excreta of lambs, goats, and kids fed white sweet clover growing on fly ash. *J Agric Food Chem* 26:847-852.
- Furr AK, Parkinson TF, Heffron CL, Reid JT, Haschek WM, Gutenmann W, Pakkalo IS, Lisk DJ 1978b Elemental content of tissues of sheep fed rations containing coal fly ash. *J Agric Food Chem* 26:1271-1275.
- Gburek WJ, Sharpley AN, Heathwaite AL, Folmar GJ 2000 Phosphorus management at the watershed scale: A modification of the phosphorus index. *J Environ Qual* 29:130-139.
- Gray CA, Paulschwab A 1993 Phosphorus-fixing ability of high pH, high calcium coal-combustion, waste materials. *Water Air Soil Poll* 69:309-416.
- Greene TW 1988 Wood Ash Disposal and Recycling Source Book. Prepared for the Coalition of Northeast Governors by OMNI Environmental Services, Ore., FL, USA.
- Green JB, Manahan SE 1978 Determination of acid-base and solubility behavior of lignite fly ash by selective dissolution of mineral acids. *Anal Chem* 50:1975-1984.
- Hart JF 1986 Using flyash as a bulking agent. *Biocycle* 27: 28-34.
- Hayden TW, Comstock EG 1975 Use of activated charcoal in acute poisoning. *Clin Toxicol* 8:515-521.
- Haynes BS, Neville M, Quann RJ, Sarofim AF 1982 Factors governing the surface enrichment of fly ash in volatile trace species. *J Coll Inter Sci* 87:266-271.
- Hecht NZ, Duvall DS 1975 Characterization and Utilization of Municipal and Utility Sludges and Ashes. Vol. III. Utility Coal Ash, Environ. Prot. Technol. Services, EPA-670/2-75-033c. USEPA.
- Hollis JF, Keren R, Gal M 1988 Boron release and sorption by fly ash as affected by pH and particles size. *J Environ Qual* 17:181-187.
- Iler RK 1979 Silica gels, powders. In *The Chemistry of Silica*, ed Iler, R.K. Wiley, New York, USA. pp. 462-469.
- Jackson BP, Miller WP, Schumann AW, Sumner ME 1999

- Trace element solubility from land application of fly ash/organic waste mixtures. *J Environ Qual* 28:689-693.
- Juliano BO 1985 Rice hull and rice straw. In *Rice: Chemistry and Technology*, ed Juliano, B.D., Am Assoc Cereal Chem St. Paul, MN, USA.
- Juliano BO, Maningat CC, Pascual CG 1987 Properties of fraction of rice hull. *Phytochemistry* 26:3261-3267.
- Kalapathy U, Proctor A, Shultz J 2000a A simple method for production of pure silica from rice hull ash. *Biores Technol* 73:257-265.
- Kalapathy U, Proctor A, Shultz J 2000b Silica xerogels from rice hull ash: Structure, density and mechanical strength as affected by gelation pH and silica concentration. *J Chem Technol* 75:464-469.
- Kalapathy U, Proctor A, Shultz J 2002 An improved method for production of silica from rice hull ash. *Biores Technol* 85: 285-293.
- Kamath SR, Proctor A 1998 Silica gel from rice hull ash: Preparation and characterization. *Cereal Chem* 75:484-491.
- Khanna PK, Raison RJ, Falkiner KA 1994 Chemical properties of ash derived from eucalyptus litter and its effects on forest soils. *For Ecol Manage* 66:107-113.
- Kopsick DA, Angino EE 1981 Effect of leachate solutions from fly ash and bottom ash on ground water quality. *J Hydrology* 54:341-348.
- Lacey RE, Mukhtars S, Carey JB, Ullman JL 2004 A review of literature concerning odors, ammonia, and dust from broiler production facilities: I. Odor concentrations and emissions. *J App Poul Res* 13:500-508.
- Lander CH, Moffitt D, Alt K 2000 Nutrients available from livestock manure relative to crop growth requirement. USDA/NRCS. In *Proceedings 2000 National Poultry Waste Management Symposium*. Ed. Bock, B.R., Economic and technical feasibility of energy production from poultry litter. Auburn University Printing service, Auburn University, AL 36849, USA. pp. 133-148.
- Lemunyon JL, Gilbert RG 1993 The concept and need for a phosphorus assessment goal. *J Prod Agric* 6:483-491.
- Leytem AB, Sims JT, Coale FJ, Sharpley AN, Gburek WJ 1999 Implementing a phosphorus site index for the Delmarva Peninsula: Challenges and research needs. In *1999 Agronomy Abstracts*. ASA, Madison, WI, USA. pp. 336-345.
- Liem H, Sandstrom M, Carne A, Blomqvist L, Thurenius B, Rydevik U 1983 Studies on the leaching and weathering processes of ashes formed from combustion of peats and biomasses. *Statens Naturvardsver PM 1775* (In Swedish with English Summary), National Environmental Protection Board, Solma, Sweden.
- Liguria Region 1988 Preliminary Liguria Region ILRES-CESEN unpublished report on 'Studio di fattibilita sulle capacita di assorbimento, da parte del contesto esterno, delle ceneri di risulta prodotte dalle centrali termoelettriche a carbone in Liguria', Genoa, Italy.
- Logsdon G 1989 Odor control with bioash. *Biocycle* 30:30-37.
- Luan TC, Chou TC 1990 Recovery of silica from the gasification of rice husks/coal in the presence of a pilot flame as a modified fluidized bed. *Ind Eng Chem Res* 29:1922-1929.
- Martens D 1971 Availability of plant nutrients of fly ash. *Compost Sci* 12:15-23.
- Mattigod SV, Rai D, Eary LE, Ainsworth CC 1990 Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel residues. I. Review of the major elements. *J Environ Qual* 19:188-195.
- Muir F, Leach RM, Jr., Heinrichs BS 1990 Bioavailability of phosphorus from broiler litter ash for chicks. *Poul Sci* 69: 1845-1853.
- Mulhern DW, Robel RJ, Furness JC, Hensley DL 1989 Chemical species in fly ash from coal-burning power plants. *J Environ Qual* 18:285-293.
- Nahm KH 2004 Additives to reduce P excretion and P solubility in poultry and swine manure. *Aust J Exp Agr* 44: 717-725.
- Natusch DFS, Wallace JR, Evans CA 1974 Toxic trace elements preferential concentration in respirable particles. *Sci* 183: 202-209.
- Naylor LM, Schmidt EJ 1986 Agricultural use of wood ash as a fertilizer and liming material. *Tappi J* 69:114-122.
- Ohno T, Erich MS 1990 Effect of wood ash application on soil pH and soil test nutrient levels. *Agric Ecosyst Environ* 32: 223-231.
- O'Reilly SE, Sims JT 1995 Phosphorus adsorption and desorption in a sandy soil amended with high rates of coal fly ash. *Commun. Soil Sci Plant Anal* 26:2983-2991.

- Peloso A, Rovatti M, Ferraiode G 1983 Fly ash as adsorbent material for toluene vapours. *Res Cons* 10:211-218.
- Proctor A, Clark PK, Parker C 1995 Rice hull ash performance under simulated commercial soy oil bleaching conditions. *J Am Oil Chem Soc* 72:459-467.
- Raask E 1969 Fusion of silicate particles in coal flames. *Fuel* 48:366.
- Raman KP, Walawender WP, Fan LT 1980 Gasification of feedlot manure in a fluidized bed reactor. The effect of temperature. *Ind Eng Chem Process Des Dev* 19:623-631.
- Ramsden AR, Shibaoka M 1982 Characterization and analysis of individual fly-ash particles from coal-fired power stations by a combination of optical microscopy, electron microscopy and quantitative electron microprobe analysis. *Atmos Environ* 16:2191-2201.
- Rosenfeld PE 1999 Characterization, quantification and control of odor emissions from biosolids application to forest soil. Ph.D. Dis., Univ. Of Washington, Seattle, WA, USA.
- Rosenfeld PE, Henry CL 2000 Wood ash control of odor from biosolids application. *J Environ Qual* 29:1662-1669.
- Rowell DL 1988 Soil acidity and alkalinity. In Russell's *Soil Conditions and Plant Growth*, 11<sup>th</sup> Ed., ed Wild, E.W., Longman Scientific & Technical, Essex, England, UK and John Wiley & Sons, New York, USA.
- Roy WR, Griffin RA 1982 A proposed classification system for coal fly ash in multidisciplinary research. *J Environ Qual* 11:563-570.
- Roy WR, Thiery RG, Schuller RM, Suloway JJ 1981 Coal fly ash: A review of the literature and proposed classification system with emphasis on environmental impacts. *Environ. Geol. Notes. III. State Geol. Surv. No. 96*. Champaign, IL., USA.
- Sander ML, Andren O 1997 Ash from cereal and rape straw used for heat production: Liming effects and contents of plant nutrients and heavy metals. *Water Air Soil* 93:93-99.
- Schade GW, Crutzen PJ 1995 Emissions of aliphatic amines from animal husbandry and their reactions: Potential source of N<sub>2</sub>O and HCN. *J Atmos Chem* 22:319-326.
- Schumann AW, Summer ME 1999 Plant nutrient availability from mixtures of fly ashes and biosolids. *J Environ Qual* 28:1651-1659.
- Sharpley AN, Chapra SC, Wedepohl R, Sims JT, Daniel TC, Reddy KR 1994 Managing agricultural phosphorus for protection of surface waters: Issues and options. *J Environ Qual* 23:437-446.
- Sharpley AN, McDowell RW, Weld JL, Kleinman JA 2001 Assessing site vulnerability to phosphorus loss in an agricultural watershed. *J Environ Qual* 30:2026-2034.
- Sharpley AN, Meisinger JJ, Breeuwsma A, Sims T, Daniel TC, Schepers JS 1998 Impacts of animal manure management on ground and surface water quality. In *Effective Management of Animal Waste as a Soil Resource*, ed Hatfield, J Lewis Publ Baca Ration FI USA, pp. 1-14.
- Sims JT, Simgrd RR, Joern BC 1998 P losses in agricultural drainage: Historical perspective and current research. *J Environ Qual* 27:277-286.
- Smith RD, Campbell JA, Nielson KK 1979 Chemical characterization of finely-sized fly-ash particles. *Environ Sci Technol* 13:1107-1114.
- Someshwar AV 1996 Wood and combination wood-fire boiler ash characterization. *J Environ Qual* 25:962-970.
- Stewart BR, Daniels WL, Jackson ML 1997 Evaluation of leachate quality from codisposed coal fly ash and coal refuse. *J Environ Qual* 26:1417-1423.
- Stout BA 1982 Conversion of biomass to fuel and chemical raw material *Experientia* 38:145-153.
- Stout WL, Sharpley AN, Gburek WL, Pionke HB 1999 Reducing phosphorus export from croplands with FBC fly ash and FGD gypsum. *Fuel* 78:175-183.
- Stout WL, Sharpley AN, Pionke HB 1998 Reducing soil phosphate solubility with coal combustion by-products. *J Environ Qual* 27:111-119.
- Stout WL, Sharpley AN, Landa J 2000 Effectiveness of coal combustion by-products in controlling phosphorus export from soils. *J Environ Qual* 29:1239-1244.
- Sun L, Gong K 2001 Silicon-based materials from rice husks and their applications. *Inc Eng Chem Res* 40:5861-5868.
- Tan KH 1994 *Environmental Soil Science*, Marcel Dekker, Inc., New York, USA. pp. 241-249.
- Theis TL, Wirth JL 1977 Sorptive behavior of trace metals on fly ash in aqueous systems. *Environ Sci Technol* 11:1096-1103.
- Thomann RV, Mueller JA 1987 *Principles of Surface Water Quality Modeling and Control*. Harper Collins Publ., New

- York, USA.
- Toth JD, Zhang G, Dou Z, Ferguson JD 2001a Reducing phosphorus solubility in animal manures using chemical amendments. In 2001 Joint Seminar of ADAS, AASA and APSA 80 (Suppl. 1), p. 251.
- Toth JD, Zhang G, Dou Z, Ferguson JD 2001b Reducing readily soluble phosphorus forms in animal manures using chemicals. In Inter. Symp. Add. Anim. Prod. and Environmental Issues. Sheraton Imperial, Research Triangle Park, NC, USA. Oct. 3-5, 2001.
- Tulonen T, Arvola L, Ollila S 2002 Limnological effects of wood ash application to the subcatchments of boreal, humic lakes. *J Environ Qual* 31:946-953.
- Vincini M, Carini F, Silva S 1994 Use of alkaline fly ash as an amendment for swine manure. *Bio Technol* 49:213-221.
- Vinyard DL, Bates MH 1979 Fly ash collected from electrostatic precipitators: Microcrystalline structures and the mystery of the spheres. *Water, Sewage Works* 126:62-69.
- Yun SC 2005 Guide for use and application of animal experiment. National Livestock Research Institute, RDA, South Korea.
- Wadge A, Hutton M, Peterson PJ 1986 The concentrations and particle size relationships of selected trace elements in fly ashes from U.K. coal-fired power plants and a refuse incinerator. *Sci Total Environ* 54:13-21.
- Warren CJ 1992 Some limitations of sluiced fly ash as a liming agent for acidic soil. *Waste Manag Res* 10:317-325.
- Warren CJ, Dudas MJ 1984 Weathering processes in relation to leachate properties of alkaline fly ash. *J Environ Qual* 13:530-538.
- Warren CJ, Dudas MJ 1985 Formation of secondary minerals in artificially weathered fly ash. *J Environ Qual* 14:405-409.
- Zhang H, Dao TH, Basta NT, Dayton EA, Daniel TC 2002 Remediation techniques for manure nutrient loaded soils. In Proceedings of Natl. Center for Manure and Anim. Waste Manag., Raleigh, NC, USA.