

# INTERPHASE CORRELATIONS OF CONCENTRATIONS OF TRACE AND MAJOR ELEMENTS OBTAINED BY SEQUENTIAL EXTRACTION OF "NIKOLA TESLA A" POWER PLANT COAL ASH

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## Abstract

Six composite samples of filter coal ash from "Nikola Tesla A" power plant located in Obrenovac near Belgrade were subjected to the sequential extraction procedure. Five extractants were applied (in the following order): distilled water (for the adsorbed fraction), 1 M ammonium acetate (ion-exchangeable fraction), 0.2 M ammonium oxalate / 0.2 M oxalic acid (in order to reduce and dissolve the fraction bound to (oxy)hydroxides of iron and manganese, but also some aluminosilicates), an acidic solution of  $H_2O_2$  (for the organic fraction), and 6 M HCl (which was shown to dissolve a significant portion of the aluminosilicate fraction). While intraphase correlations, e.g. correlations between concentrations of elements extracted in the phases where the inorganic matrix is being dissolved (third and fifth phase of sequential extraction) can provide information about the composition of the mentioned matrix of coal ash particles, the interphase correlations, e.g. correlations between concentrations of mobile (first and second) phases and phases where inorganic matrix (third and fifth) are dissolved, can give the information about preferable sorption of certain elements to inorganic constituents of coal ash particles. Such correlational analysis of obtained extractational results showed that majority of adsorbed and ion-exchangeable elements were preferably connected with different silicates, aluminates and compounds of iron that were soluble in the third and fifth phase of the sequential extraction.

## Introduction

Coal is a complex combination of organic materials (those that burn) and inorganic materials (those that produce ash). The inorganic materials can be further subdivided into mineral grains and organically associated inorganics. The mineral grains consist of particles ranging in size from microscopic to sand-sized and even larger-sized materials. Both the size and chemistry of these mineral particles control where the ash will end up in a combustion system. A growing human population, reliant on coal combustion for electricity generation, will increase the amount of this effluent produced in the future. Until recently, the potential dangers of coal ash to wildlife have been underestimated, but relatively recent studies indicate that coal ash may pose significant physiological and ecological problems that warrant attention from the scientific and regulatory communities. Organisms inhabiting coal ash basins, downstream areas, and nearby terrestrial habitats accumulate high levels of trace elements in their tissues. Moreover, chronic exposure to coal ash results in impairment of multiple physiological and developmental systems in amphibians, reptiles, and aquatic invertebrates. Observed effects include deformities, abnormal behaviours, endocrine disruption, modified energy budgets, and inhibited metamorphosis (1).

The physical and chemical properties of this industrial waste product, in general, are quite variable, as they are influenced by coal source, particle size, type of coal burning process, and degree of weathering. The fly ash consists of many small (0.5 - 100  $\mu\text{m}$  diameter) glass-like particles of a remarkably spherical character, a finely crystalline material or as a more coarsely crystallised ceramic, depending on composition (2). The bulk of the fly ash consists of silicon, aluminium, calcium oxide, and iron oxide. It also contains organic residues including polychlorinated dibenzodioxins and dibenzofurans (3).

Coal burning is major energy source in ex-Yugoslavia, contributing more than two thirds of total energy needs of the country. There are nine power plants in ex-Yugoslavia, eight of them are located in Serbia, while one is in Montenegro. Though coal is important as energy source, its translation to energy yields large amount of coal ash that is only marginally used, thus representing one of the largest environmental problems in the country. Although leaching of inorganic constituents from Yugoslav power plant's coal ash has been widely recognised as threat to surrounding soil and ground and surface waters, the analysis of potential influence was usually limited to trace elements (4-6).

## Experimental

In this work, six composite samples of coal ash obtained by coal burning in power plants "Nikola Tesla A" were subjected to extraction procedures with extractants dissolving different constituents. Five extractants were applied (in the following order): distilled water (for the adsorbed fraction), 1 M ammonium acetate (ion-exchangeable fraction), 0.2 M ammonium oxalate / 0.2 M oxalic acid (in order to reduce and dissolve the fraction bound to (oxy)hydroxides of iron and manganese), an acidic solution of H<sub>2</sub>O<sub>2</sub> (for the organic fraction), and 6 M HCl (which was shown to dissolve a significant portion of the aluminosilicate fraction). Obtained concentrations of trace and major elements in phases of sequential extraction where inorganic matrix is being dissolved, e.g. third and fifth (discussed from geochemical standpoint in (7)), were then statistically analysed in order to establish composition of inorganic matrix (8).

## Results

Correlational parameters (correlational coefficient R and significance of correlation p) obtained by correlational analysis of concentrations of trace and major elements leached in the first and second phase of sequential extraction of coal ash on one, and concentrations of major elements leached in the third and fifth phase of sequential extraction of coal ash "Nikola Tesla A" power plant are shown in Tables 1 and 2.

Table 1: Correlational parameters (correlational coefficient R and significance of correlation p) obtained by analysis of concentrations of trace and major elements leached in the first phase of sequential extraction and concentrations of major elements leached in the third and fifth phase of sequential extraction of coal ash "Nikola Tesla A" power plant. Correlations that are shaded represent those with significance of correlation  $p \leq 0.05$ .

		Mg	Al	Si	K	Fe	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Mg	R	0.68	-0.93	0.94	0.38	0.85	0.92	0.54	0.43	0.70	0.88	0.90	0.36	0.85
	V p	0.14	0.01	0.01	0.46	0.03	0.01	0.27	0.40	0.12	0.02	0.02	0.48	0.03
Al	R	0.50	-0.85	0.94	0.45	0.82	0.96	0.57	0.43	0.79	0.97	0.93	0.45	0.88
	V p	0.32	0.03	0.00	0.28	0.05	0.00	0.24	0.39	0.06	0.00	0.01	0.37	0.02
Si	R	0.43	-0.72	0.94	-0.05	0.67	0.85	0.66	0.23	0.70	0.97	0.98	0.52	0.72
	V p	0.39	0.11	0.00	0.93	0.14	0.03	0.15	0.66	0.12	0.00	0.00	0.29	0.10
K	R	0.32	-0.42	0.77	-0.05	0.35	0.57	0.60	-0.09	0.40	0.80	0.86	0.48	0.40
	V p	0.53	0.41	0.07	0.93	0.50	0.24	0.21	0.86	0.43	0.06	0.03	0.33	0.44
Fe	R	0.62	-0.81	0.89	0.65	0.99	0.91	0.57	0.73	0.84	0.76	0.80	0.61	0.93
	V p	0.19	0.05	0.02	0.16	0.00	0.01	0.24	0.10	0.04	0.09	0.06	0.20	0.01
Mg	R	0.57	-0.01	0.04	0.03	0.28	-0.17	0.13	0.31	-0.10	-0.37	-0.08	0.30	-0.05
	III p	0.24	0.99	0.94	0.95	0.60	0.75	0.81	0.55	0.85	0.47	0.88	0.56	0.93
Al	R	0.08	-0.52	0.58	-0.09	0.16	0.54	0.40	-0.26	0.32	0.80	0.70	0.01	0.34
	III p	0.87	0.29	0.22	0.86	0.76	0.27	0.43	0.62	0.54	0.07	0.12	0.99	0.52
Si	R	0.19	-0.64	0.71	0.11	0.38	0.74	0.37	-0.02	0.50	0.91	0.79	0.11	0.58
	III p	0.74	0.17	0.11	0.84	0.46	0.09	0.46	0.96	0.31	0.01	0.06	0.83	0.23
K	R	0.22	-0.59	0.65	-0.14	0.21	0.53	0.51	-0.27	0.30	0.80	0.76	0.04	0.32
	III p	0.67	0.21	0.16	0.80	0.69	0.28	0.30	0.60	0.57	0.06	0.08	0.94	0.54
Fe	R	-0.07	-0.55	0.39	0.53	0.43	0.38	0.74	0.32	0.58	0.45	0.38	0.20	0.36
	III p	0.90	0.26	0.45	0.28	0.40	0.46	0.10	0.53	0.22	0.38	0.45	0.71	0.49

## Discussion

As it can be seen from tables 1 and 2, there are significant correlations of certain fractions of trace and major elements that are easily extracted (adsorbed, e.g., first and ion-exchangeable, e.g., second) with some fractions of certain major elements that are portion of inorganic matrix of coal ash particles. Those correlations can possibly mean that during processes that are responsible for the formation of adsorbed and ion-exchangeable fractions of some elements, there is preference during mentioned formation of certain elements to some portion of inorganic matrix. The composition of matrix is discussed in (8), and, resulting from intraphase correlations of concentrations of elements leached in third and fifth phase of extraction, it was found that there are at least seven important constituents of coal ash particles that are being dissolved in these two phases of extraction. In fifth phase of sequential extraction are thus leached aluminosilicates of magnesium (carriers of arsenic, copper and chromium), silicates of potassium (carriers of lead and nickel), mixed aluminates of magnesium and iron (associates of arsenic, copper and chromium), aluminosilicates that are not

Table 2: Correlational parameters (correlational coefficient R and significance of correlation p) obtained by analysis of concentrations of trace and major elements leached in the second phase of sequential extraction and concentrations of major elements leached in the third and fifth phase of sequential extraction of coal ash "Nikola Tesla A" power plant. Correlations that are shaded represent those with significance of correlation  $p \leq 0.05$ .

		Mg	Al	Si	K	Fe	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Mg	R	0.93	0.51	0.56	0.36	0.84	0.60	0.90	0.86	0.84	0.57	-----	0.78	-0.07
V	p	0.01	0.30	0.24	0.49	0.04	0.20	0.01	0.03	0.04	0.24	-----	0.06	0.90
Al	R	0.92	0.51	0.58	0.44	0.85	0.65	0.91	0.94	0.91	0.68	-----	0.65	-0.19
V	p	0.01	0.30	0.22	0.39	0.03	0.16	0.01	0.00	0.01	0.14	-----	0.16	0.72
Si	R	0.88	0.6	0.70	0.58	0.87	0.76	0.88	0.99	0.97	0.73	-----	0.61	-0.05
V	p	0.02	0.18	0.12	0.23	0.02	0.08	0.02	0.00	0.00	0.10	-----	0.20	0.92
K	R	0.67	0.66	0.70	0.58	0.72	0.75	0.64	0.87	0.88	0.63	-----	0.44	0.12
V	p	0.15	0.15	0.12	0.23	0.11	0.08	0.17	0.02	0.02	0.18	-----	0.38	0.81
Fe	R	0.74	0.18	0.27	0.20	0.65	0.29	0.88	0.71	0.66	0.29	-----	0.72	-0.19
V	p	0.08	0.73	0.60	0.70	0.16	0.58	0.02	0.11	0.16	0.58	-----	0.11	0.72
Mg	R	-0.19	-0.36	-0.38	-0.36	-0.25	-0.49	-0.00	-0.34	-0.34	-0.77	-----	0.37	0.38
III	p	0.72	0.48	0.46	0.48	0.63	0.33	0.99	0.50	0.52	0.07	-----	0.47	0.46
Al	R	0.74	0.82	0.85	0.69	0.80	0.93	0.57	0.85	0.85	0.97	-----	0.30	0.00
III	p	0.09	0.04	0.03	0.13	0.06	0.01	0.24	0.03	0.03	0.00	-----	0.56	0.99
Si	R	0.82	0.72	0.76	0.57	0.83	0.86	0.67	0.92	0.92	0.94	-----	0.37	-0.18
III	p	0.04	0.11	0.08	0.24	0.04	0.03	0.15	0.01	0.01	0.00	-----	0.47	0.74
K	R	0.81	0.90	0.92	0.76	0.87	0.97	0.64	0.87	0.87	0.94	-----	0.44	0.16
III	p	0.05	0.02	0.01	0.08	0.02	0.00	0.17	0.02	0.02	0.01	-----	0.38	0.76
Fe	R	0.59	0.38	0.53	0.80	0.64	0.47	0.69	0.44	0.29	0.61	-----	0.38	0.09
III	p	0.22	0.45	0.28	0.06	0.17	0.35	0.13	0.38	0.57	0.20	-----	0.46	0.86

containing magnesium (carriers of lead and zinc) and compounds of iron other than mixed aluminates (carriers of manganese and zinc). In the third phase of sequential extraction aluminosilicates of potassium (carriers of copper) and compounds of iron (carriers of zinc) are leached.

According to correlation coefficients shown in tables 1 and 2, most of these compounds represent preferred foundation for sorption of adsorbed and ion-exchangeable fractions of most of major and trace elements. Potassium and cadmium are the only two elements having no adsorbed and ion-exchangeable fractions that are significantly correlated with major elements leached in third and fifth phase of sequential extraction. This probably means that mentioned fractions of these two elements are either bound to organic fraction of coal, or are bound without any selectivity to different substrates.

Aluminosilicates of magnesium dissolved in the fifth phase of sequential extraction are preferred for adsorbed fraction of silicon, chromium, zinc and arsenic, as well as ion-exchangeable portions of magnesium, iron, manganese, copper and nickel- all these elements are significantly correlated with concentrations of silicon, aluminum and magnesium that are leached in the fifth phase of extraction. Other three important substrates of trace elements dissolved in the last phase of extraction are also important matrix for sorption of mobile fractions of trace and major elements: silicates of potassium are host of adsorbed arsenic and ion-exchangeable nickel and copper, mixed aluminates of iron and magnesium are associated with adsorbed silicon, iron, chromium and lead, as well as ion-exchangeable manganese, while compounds of iron are "host" of adsorbed fraction of copper. It is interesting to notice that remaining postulated substrate dissolved in the fifth phase of sequential extraction (8) - aluminosilicates that are not containing magnesium, are not "target" for preferred sorption of trace and major elements.

Out of two postulated constituents of coal ash particles that are dissolved in the third phase of sequential extraction (8), only one, aluminosilicates of potassium, is associated with ion-exchangeable fractions of chromium, nickel, copper and zinc. Other postulated substrates, compounds of iron, are not, according to correlational analysis, preferred form for sorption of mobile fractions of examined trace and major elements. However, interphase correlational analysis points to the possibility of existence of three less complicated substrates than postulated aluminosilicates of potassium. Ion-exchangeable silicon and aluminum are significantly correlated with concentrations of potassium and aluminum, while ion-exchangeable iron is significantly correlated with concentrations of potassium and silicon extracted in the third phase. Also, significance of correlation between the concentrations zinc leached in the first and silicon leached in the third phase of extraction is smaller than 0.05. This point to the possibility that aluminates of potassium and silicates of potassium, that are associated

with ion-exchangeable silicon and aluminum (aluminates of potassium) or ion-exchangeable iron (silicates of potassium), as well as forms of silicon not associated with potassium or aluminum (preferred sorbent of zinc) also do exist.

#### **Literature**

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