GEOCHEMICAL MARKERS OCCURRENCE AND DISTRIBUTION IN FLY ASH FROM COAL-FIRED BOILERS

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Introduction

Combustion of coal in different types of boilers and stoves for energy and heat production leads to emission into the atmosphere in the form of large amounts of gaseous pollutants and particulate. It has been proven that the influence of pollutants from coal furnaces in both atmospheric and indoor air is dangerous to health. Chemical analyses and biological tests identify polycyclic aromatic hydrocarbons (PAHs) as a group of compounds, which determine the mutagenic and carcinogenetic effects of the emission from coal combustion (IARG 2012). Research into the participation of the emission sources in the air pollution with PAHs has been conducted over a long period of time. In the process, the profiles of the PAHs present in the particulate matter have been compared, as well as used, for example, to determine diagnostic ratios based on the analysis of PAHs. However, the research conducted so far did not resolve the issue concerning each of the main PAH emission sources, since PAHs are subjected to biological- and photo- degradative decomposition. The breakthrough was to use geochemical markers, which are substances associated with PAHs but are much more stable. This provides information on the origin of organic matter, as well as the way in which migration and degradation occur in the environment. Many of these geochemical markers have a link with the kind of fuel combusted (bituminous coal, lignite, hydrocarbon engine fuels, biomass, wood).

The objective of the research was to assess the co-occurrence of PAHs and biomarkers in the fly ash emitted from bituminous coal and co-firing of bituminous coal and forest biomass to determine the level and profiles of the selected PAHs and biomarkers with consideration of the combustion mode and the degree of coalification of the fuel. Organic compounds extracted from fly ash emitted various power plants combusting bituminous coal or bituminous coal/biomass fuel in different types of boilers - travelling grate water and steam, pulverized coal-fired steam, and fluidized bed combustion boiler were analyzed by gas chromatography-mass spectrometry (GC-MS) whereas for PAH investigation on the GC-FID was used.

Results

The following compound groups from combusted bituminous coal have been identified in the PM extracts: *n*-alkanes and *iso*-alkanes, acyclic isoprenoids, mostly pristane (Pr) and phytane (Ph), steranes, in some cases accompanied by diasteranes, and tri- and pentacyclic triterpenoids. Diterpenes were present in a small number of extracts in low concentrations, which is a common feature in Upper Silesia coals. Among aromatic hydrocarbons PAHs and their alkyl derivatives were identified. Apart from biomarkers, compounds of biochemical origin were found, particularly in fly ash from co-firing biomass/bituminous coal, in which they are the dominant organic compound group. Among them were long-chain aliphatic alcohols, ketones, methyl esters of fatty acids, farnesol, levoglucosan, squalene, vitamin E, β-sitosterol, and phenol derivatives, such as cresols, xylenols, and guaiacol.

Investigated fly ash, derived from bituminous coal combustion in a variety of boilers, contained an average of from 21.4 to 65.2 µg of the sum of 16 PAHs in 1g. In the case of bituminous coal and forest biomass co-firing in fluidized bed combustion boiler, there was 110.85 µg/g of the total PAHs; BbF>Phe>DBA>Fl in the largest quantities and toxic equivalence was as high as 103.2 µg/g.

There is an obvious influence of the boiler type on *n*-alkane distributions, resulting in significant changes compared to bituminous coal extracts. The distinguishing feature of travelling grate steam boiler fly ash is the higher percentage of lightest *n*-alkanes (~6-9%), compared to 1-2% the others. The *n*-alkanes distributions fly ash, apart from that from biomass combustion, showed only slight odd-over-even carbon atom number predominance with the carbon preference index (CPI) values in the range of 1.00 to 1.56, corresponding to that bituminous coals. Fly ash from the modern fluidized bed combustion boiler was particularly poor in all geochemical compounds. There was a significant decrease of Pr/Ph values for (0.06 on aver.) for this boiler, possibly due to more advanced thermal destruction of lighter Pr than Ph. Hopanes and moretanes (*m/z* = 191) occurred in fly ash extracts in the range of 18α(H)-22,29,30-trisnorneohopane (Ts) to 17α(H),21β(H)-29-pentakishomohopane ($C_{35}\alpha\beta$); however, in most cases, the distributions ended at 17α(H),21β(H)-29-trishomohopane ($C_{33}\alpha\beta$) as is common in most humic coals and kerogen III. The specific feature of traveling grate boiler fly ash is the absence of Ts, as well as the occasional removal of Tm. There is no real influence of the boiler type on relative percentage contents of C_{29}-C_{30}-C_{31} hopanes. Distribution of alkyl aromatic hydrocarbons, in particular those of higher molecular weight, were well preserved what enabled to calculate their ratios. However, the MPI-1 values for some fly ash are clearly too low, perhaps due to formation of phenanthrene.

Conclusions

Fly ash from coal and biomass co-firing contains the highest PAH concentrations, as well as indicates the highest TEQ values among all boilers investigated. It is a significant problem from a municipal and health hazard point of view. Fly ash from bituminous coal combustion in different types of boilers is rich in four-ring PAHs (approximately 70%), whereas the source fuel (i.e., raw bituminous coal) is rich in three-ring PAHs. Studies have shown that the distributions of geochemical markers and biochemical markers, as well as the distribution of the majority of aromatic hydrocarbons and their aliphatic derivatives in fly ash, which is emitted from a variety of boilers combusting bituminous coal and composite fuel, show a significant similarity to combusted coal. It has been found that the thermal changes in the distributions and presence of biomarkers, caused by combustion, are small and mainly affect compounds of low molecular weight. It is possible that high molecular weight compounds survived the high temperature process when adsorbed in unburned or coked coal and/or biomass particles included in the dust emitted. The results confirm the thesis concerning the general preservation of geochemical features of source fuel in organic matter of fly ash, particularly with respect to compounds of high molecular mass, and indicate the usefulness of these compounds in research on the type of emission sources of particulate matter into the air.

References

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