Investigation of Cd and Zn Isotope Signatures of Coal Combustion Products

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ABSTRACT

Coal combustion is a widely applied industrial process with many potential environmental impacts. In particular, its extensive use for energy production creates large amounts of coal combustion products (CCPs). These CCPs may contain high concentrations of toxic metals, such as Cd and Zn, which can be harmful to environments and human health. During coal combustion, physical processes such as evaporation and condensation can redistribute Cd and Zn among CCPs and fractionate their isotopes. These Cd and Zn isotopic signatures have the great potential to be used to mark anthropogenic metal inputs to the environment.

Here, we characterized the distribution of Cd and Zn in various CCPs [bottom ash (BA), economizer fly ash (EFA) and fly ash (FA)], parent feed coal (FC) and pulverized coal (PC) by mapping Zn and Pb on CCPs with electron-microprobe (EMP) analysis. Enrichment of these metals on the surface of the CCP particles was observed. We further analyzed Cd and Zn isotopic compositions of these CCPs. Cd and Zn isotope analyses in bulk CCP samples reveal an unexpected finding: heavy Cd isotope signatures were observed in FA samples ($\delta^{114}Cd$ = -0.39 to +0.47‰) relative to BA samples (-0.75 to -0.52‰). Zn isotope signatures ($\delta^{66}Zn$) show similarly that heavier Zn isotopes are enriched in FA samples (0.07 to 1.02‰) relative to BA samples (-0.52 to -0.07‰). An initial explanation is that isotope fractionation (i.e. condensation) of heavy Cd and Zn onto the fine FA begins in the boiler and continues as the FA moves downstream along with the Cd and Zn vapor. Transport of FA and heavy Cd and Zn out of the boiler leaves relatively lighter Cd and Zn vapor to precipitate on BA. Fine FA also provides a larger surface area for condensation to occur. To assess potential fractionation processes from the coals and CCPs to the natural environment, Cd isotope signatures in products from sequential leaching experiments (DI water, diluted HNO3, acetic acid, hydroxyl ammonium chloride and H_2O_2 followed by ammonium acetate) were also investigated. Low temperature ashed FC and PC samples show a narrow range of $\delta^{114}Cd$ and $\delta^{66}Zn$ values after leaching with 5% HNO3 (0.26 to 1.17‰ and 0.06 to 0.52‰ respectively). A significant heavy Cd signature is observed in each sequential extraction phase in FA samples (1.1 to 7.05‰). In contrast, $\delta^{114}Cd$ values of BA samples are enriched in light Cd (-2.7 to +0.1‰). Similarly, enrichment on heavy Zn isotopes is observed in FA samples (1.57 to 3.31‰) relative to BA samples (-0.25 to +0.09‰) after leaching by 5% HNO_3.

Cd and Zn isotopic systems hence provide a useful tool for tracing anthropogenic sources of toxic metals in the environment as our study reveals significantly heavy Cd and Zn signatures associated with CCPs, probably due to condensation of heavy Cd and Zn isotopes onto fine CCP particles during cooling of flue gas after coal combustion.

RESULTS

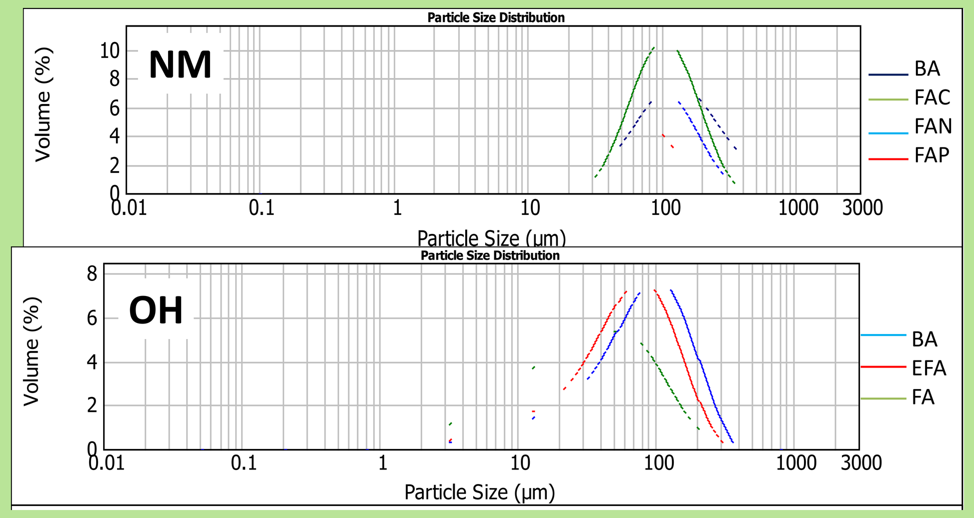

Figure 5: Particle size distribution on CCPs

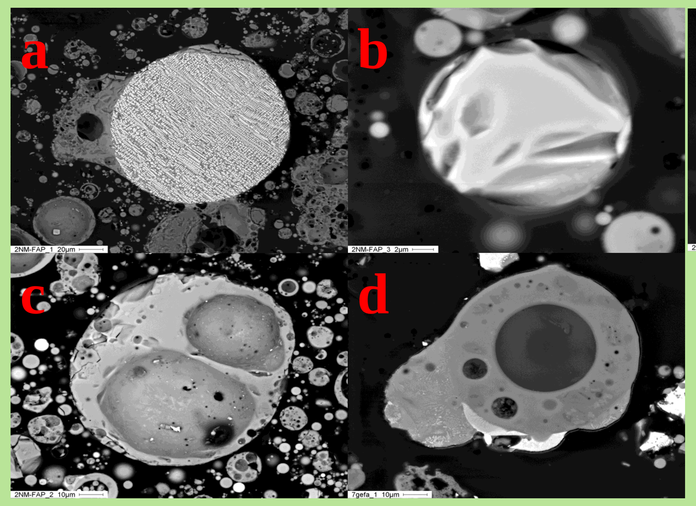

Figure 6: The 3 major types of glasses on fly ash particles by EMP analysis [(a) Fe-rich, (b) Ca-rich and (c) AlSi-rich] and (d) Fe concentrated on AlSi fly ash particle's surface

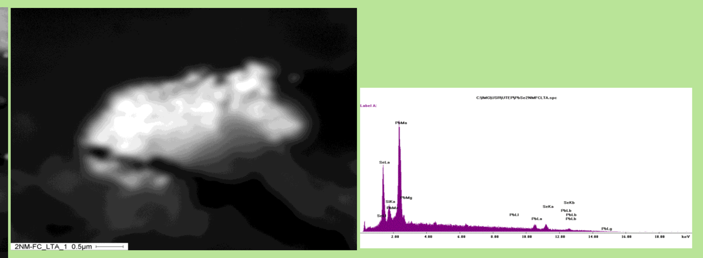
Figure 7: Pb-rich particle sitting on quartz as a PbSe phase

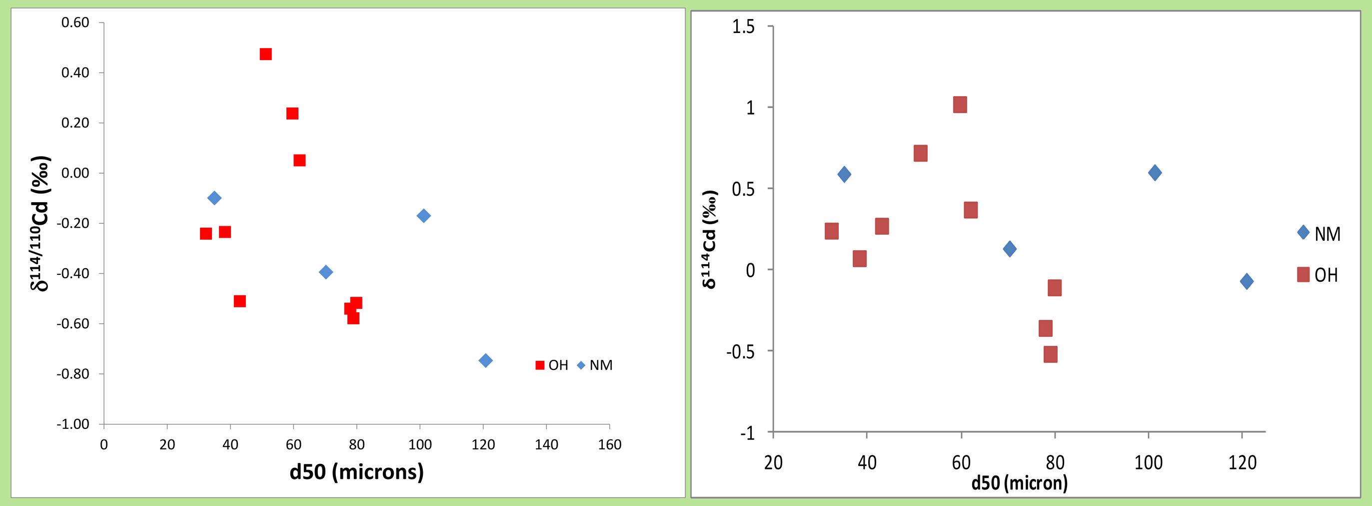

Figure 8: Particle size and Cd-Zn isotopic composition correlation on bulk CCPs

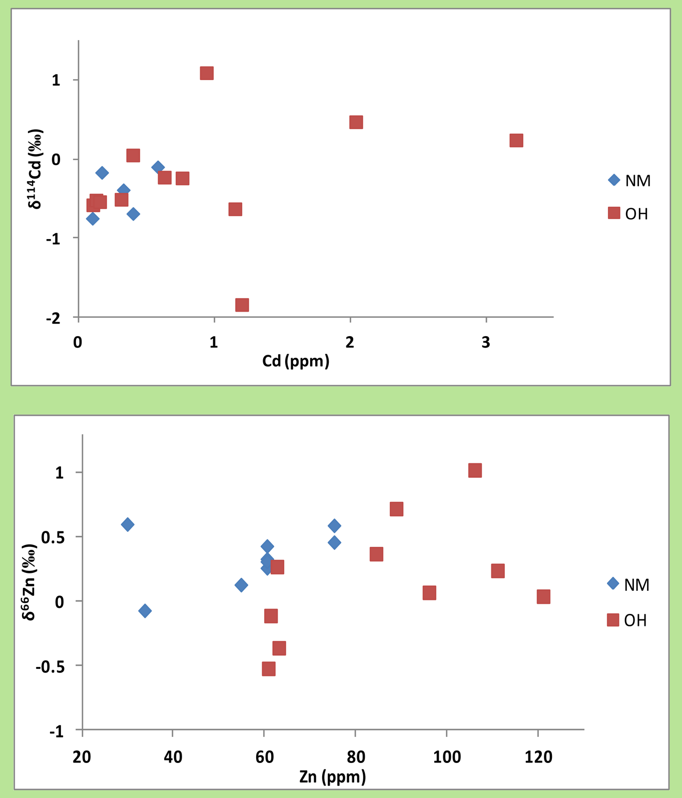

Figure 9: Cd and Zn concentration and isotopic composition correlation on bulk CCPs

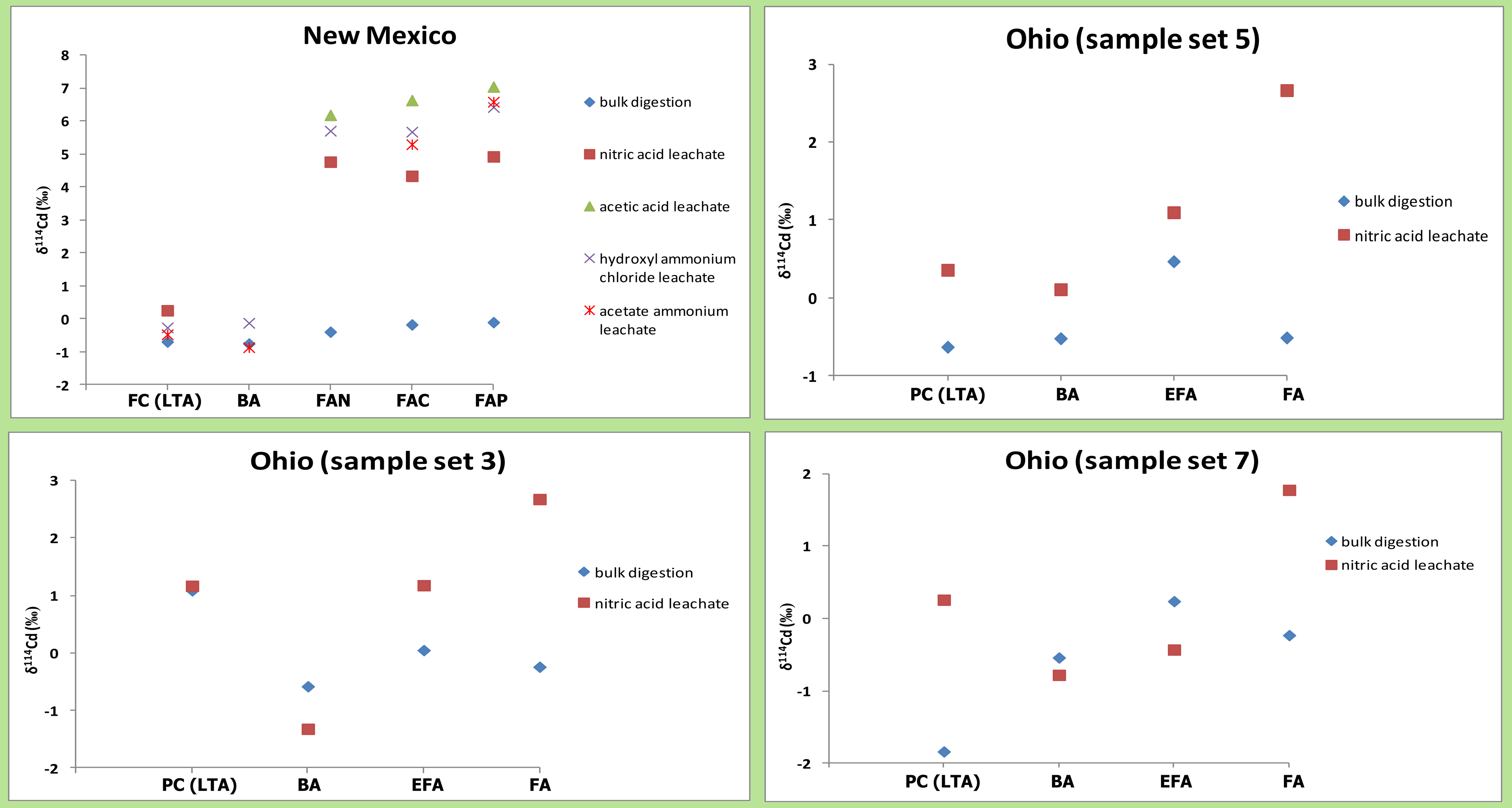

Figure 10: $\delta^{114}Cd$ values of bulk and various leaching phases on CCPs and coals

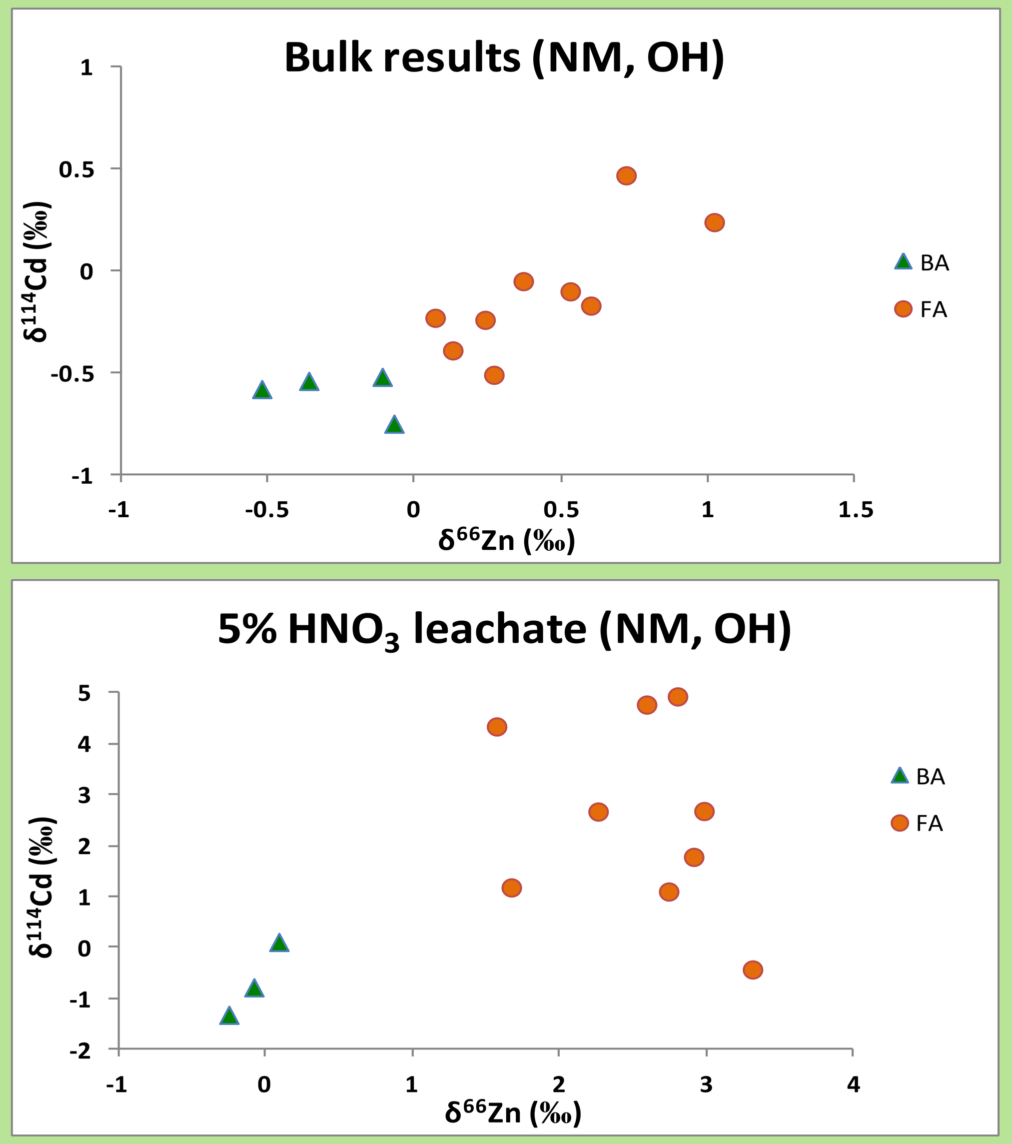

Figure 11: BA and FA sample comparison according to $\delta^{66}Zn$ and $\delta^{114}Cd$ values of bulk and 5% HNO_3 leaching phase

METHODS-SAMPLES

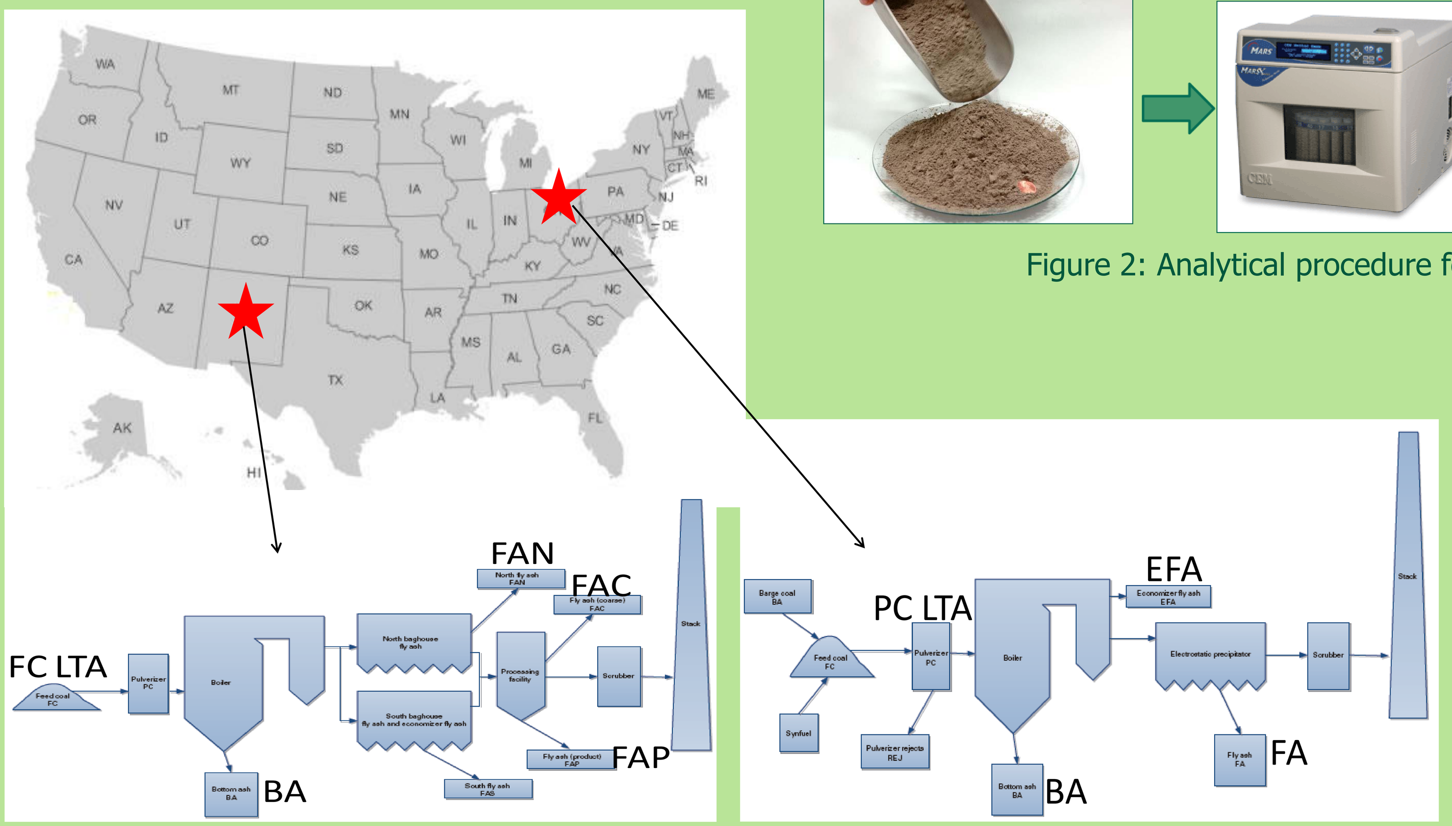

Figure 1: New Mexico and Ohio coal-fired power plants in this study and flow of coal during combustion (Affolter et al. 2011)

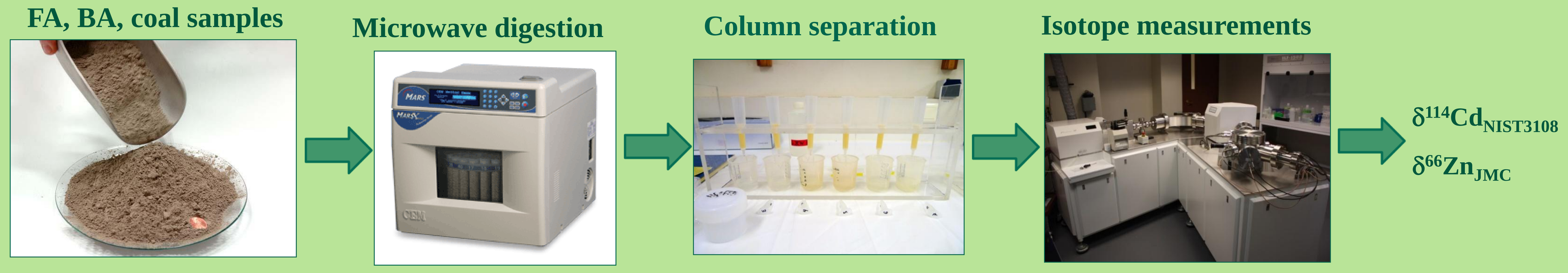

Figure 2: Analytical procedure for Cd and Zn isotopic measurements for CCP samples


Figure 3: JEOL JXA-8900R electron microprobe (USGS) and Malvern AWA-2000 particle size analyzer (UTEP)

STEP	REACTIVE	C (M/l)	pH	PHASE
1	CH3COOH	0.1		exchangeable or soluble
2	NH2OH-HCl	0.1	2.0 HNO3	redusible (Fe-Mn oxides)
3	H2O2+CH3COONH4	8.8 + 1.0	2.0 HNO3	oxidisable (sulfides)
4	Bulk digestion (HNO3, HF)			residual (silicates)

Figure 4: Sequential extraction procedure on CCPs

CONCLUSIONS

- Electron microprobe analysis showed enrichment of Zn and Pb concentrations on CCP particle's surface
- Cd and Zn isotopes fractionate and redistribute in CCPs as the flue gas cools after combustion
- Heavy Cd and Zn isotopes condensate on fine particles of CCPs such as fly ashes
- Bottom ash samples are enriched in light Cd and Zn isotopes while fly ash samples are enriched in heavy Cd and Zn isotopes
- Sequential leaching experiments reveal a significant heavy Cd and Zn signature relative to the bulk results up to 7‰ (5% HNO_3, CH_3COOH, NH_2OH-HCl, $H_2O_2+CH_3COONH_4$) and up to 3.5‰ (5% HNO_3) respectively
- Cd and Zn isotope systems may provide a useful tool for tracing anthropogenic sources of toxic metals in the environment

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