

Arsenic, cadmium, lead, and zinc in the Danville and Springfield coal members (Pennsylvanian) from Indiana

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Abstract

Arsenic, cadmium, lead, and zinc contents and distributions are discussed in two major Pennsylvanian coal beds in Indiana: the Danville Coal Member and the Springfield Coal Member. Arsenic contents of the Danville and Springfield coals show similar ranges from 0.5 to 43 ppm for the Danville Coal and 1 to 50 ppm for the Springfield Coal, with an average of 12.7 ppm for the Danville and 9.4 ppm for the Springfield Coal. Cadmium concentrations do not exceed 9 ppm, with an average of 0.4 for Danville and 0.7 ppm for the Springfield. Average Pb contents are 21.3 and 6.3 ppm, whereas Zn contents are 101 and 54 ppm for the Danville and the Springfield, respectively. The distribution of these elements varies both laterally and vertically within the coals, as functions of their mineral associations and the time of their emplacement.

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1. Introduction

Inorganic constituents in coal have an important effect on almost every aspect of coal utilization, as well as major impacts on the environment. Arsenic (As), cadmium (Cd), lead (Pb), and zinc (Zn) are among elements of environmental concern. Cases have been documented that Cd-contaminated soils in Japan caused significant human health effects (Holmgren et al., 1993), whereas high Pb levels in children in the U.S. (Millstone, 1997; Mielke, 1999; Filippelli et al., 2005) are blamed, at least partly, on Pb concentrations in the food (Holmgren et al. 1993). Paint, automobile exhausts, as well as industrial

emissions are the main sources of this element (Alloway, 2005). There is evidence for the chronic toxicological effects of As in drinking water (Smedley and Kinniburgh, 2002). It is also suggested that airborne As can give rise to health problems. Arsenic is mobilized not only through a combination of natural processes such as weathering, biologic activity, and volcanic emissions, but also through a range of anthropogenic activities. Drastic examples of poisoning by As from domestic heating of high-As coals are known from China, where more than 3000 cases have been documented (Ding et al., 2001). Coal, among other natural sources, contains these potentially toxic elements and, because they can be concentrated or liberated during coal combustions, we must understand their concentrations and distribution in coal.

The distribution of the trace elements is also important geologically because these elements can provide some

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indication about depositional and post-depositional processes. Zinc, Pb, and Cd are chalcophile elements whose high concentrations can be considered an indicator of epigenetic mineralization (Gluskoter and Lindahl, 1973; Hatch et al., 1976; Cobb et al., 1980). Zinc and Cd are usually associated with sphalerite, and Pb with galena (Finkelman, 1982) and clausthalite (PbSe; Hower and Robertson, 2003). Arsenic commonly occurs as a solid phase in pyrite (Bouska, 1981; Finkelman, 1994; Yudovich and Ketris, 2005) and, similarly to pyrite, can be syngenetic or epigenetic in origin.

The purpose of this paper is to investigate the distribution of As, Pb, Cd, and Zn within two coal beds

of major economic interest in Indiana. The major objectives of this study are: 1) to better understand depositional and post-depositional factors that influence distributions of these elements in coal and 2) discuss to what extent these elements can be removed by conventional washing.

2. Geologic setting

Coal-bearing rocks in Indiana are part of the Pennsylvanian System of the Illinois Basin. They are divided into three major stratigraphic units: the Raccoon Creek Group, the Carbondale Group, and the McLeansboro Group (Fig. 1). The Raccoon Creek Group extends

Illinois		Indiana		W. Kentucky		
McLeansboro Gp.	Mattoon Fm.	McLeansboro Gp.	Mattoon Fm.	McLeansboro Group	Mattoon Fm.	Virg.
	Bond Fm.		Bond Fm.		Bond Fm.	Missourian
	Patoka Fm.		Patoka Fm.		Patoka Fm.	
	Shelburn Fm.		Shelburn Fm.		Shelburn Fm.	
Carbondale Fm.	Danville (No.7) Jamestown	Carbondale Group	Danville (VII) Hymera (VI) Herrin Bucktown (Vb)	Carbondale Fm.	Baker (No.13) Paradise (No.12)	Desmoinesian
	Herrin (No.6)		Springfield (V)		Herrin (No.11)	
	Springfield (No.5)		Houchin Creek		Springfield (No.9)	
	Houchin Creek		Survant (IV)		Houchin Creek	
	Survant		Colchester (IIIa) Seelyville (III)		Survant (No.8)	
Raccoon Creek Group	Colchester (No.2) Dekoven Davis	Raccoon Creek Group	Unnamed Staunton Fm. coals	Raccoon Creek Group	(Mining City) No.4 Empire	Atokan
	Willis		Minshall /Buffaloville		Lead Creek/Dunbar	
	Reynoldsburg		Upper Block Lower Block		Elm Lick	
	Gentry		Mariah Hill Blue Creek		(Ice House) No.3 Foster Amos Bell	
	Caseyville Fm.		Pinnick St. Meinrad French Lick		Battery Rock Nolin	
						Morrowan

Fig. 1. Lithostratigraphy of the Pennsylvanian System in Indiana (modified from Mastalerz and Harper, 1998, and the The TriState Committee on Correlation of the Pennsylvanian System in the Illinois Basin, 2001). Although numbers of the coal beds have been abandoned in all the three states, they are included here because they are still in use in coal mines.

Table 1

Ash, sulfur, calorific value, and As, Cd, Pb, and Zn contents for the Danville and Springfield Coal Members in Indiana

	Danville			Springfield					
	Range	Average	n	Range	Average	n			
Ash (% dry)	4.9–41.1	12.3	139	4.9–30.1	11.3	311			
S (% dry)	0.3–6.0	2.6	137	0.50–7.70	4.1	338	U.S. coals average	Earth's crust average	U.S. soils
Heating value (Btu/lb, dry)	7651–13889	12304	137	8744–14025	10924	338			
As (ppm, whole coal)	0.50–43.00	12.7	33	1.00–50.00	9.4	64	24	5	Not avail.
Cd (ppm, whole coal)	0–4.85	0.4	33	0.06–9.00	0.7	44	0.47	0.18	0.005–2.0
Pb (ppm, whole coal)	1.7–75.3	21.3	38	0.69–30.00	6.3	44	11	16	0.5–135
Zn (ppm, whole coal)	9–331	101.5	38	6.6–300	54.2	44	53	40	1.5–264

Earth's crust averages are after Krejci Graf (1972), U.S. coal averages are after Finkelman (1993) and Bragg et al. (1998) and U.S. soil ranges after Holmgren et al. (1993).

from the base of the Pennsylvanian System to the base of the Seelyville Coal Member. This group consists of three formations: the Mansfield Formation, the Brazil Formation, and the Staunton Formation. Several coal beds of this group, including the Blue Creek, Mariah Hill, Lower Block, Upper Block, and Minshall/Bufalo-ville Coal Members, are of economic interest. The Carbondale Group comprises the Linton Formation, the Petersburg Formation, and the Dugger Formation. Within this group, the Danville, Hymera, and Springfield Coal Members have been of economic importance. The McLeansboro Group includes Pennsylvanian strata above the Danville Coal, but without economic importance.

Overburden thickness of the Danville Coal in Indiana ranges from 0 to more than 500 ft (~ 152 m) deep. This coal is usually from 14 to 42 in. (35–106 cm) thick, although zones of thicker coal occur in Knox, Sullivan, and Vigo counties (Conolly and Zlotin, 2000; Mastalerz et al., 2004). The total remaining resources of the Danville coal are estimated at 6.19 billion short tons (5.6 billion metric tons), and available resources at 0.83 billion short tons (0.75 billion metric tons), 0.35 billion short tons (0.32 billion metric tons) of which are available from surface mining and 0.52 billion short tons (0.47 billion metric tons) from underground mining (Conolly and Zlotin, 2000; Mastalerz et al., 2004). The overburden thickness of the Springfield Coal ranges from zero along the outcrops to more than 500 ft (~ 152 m) in Gibson and Posey counties. The thickness of this coal is usually from 42 to 63 in. (106–160 cm). The total remaining resources of the Springfield Coal are estimated at 12.00 billion short tons (10.8 billion metric tons), and available resources at 7.35 billion short tons (6.66 billion metric tons), 0.82 billion short tons (0.74 billion metric tons) of which can be surface-mined and 6.94 billion short tons (6.3 billion metric tons) mined from underground (Conolly and Zlotin, 1999; Mastalerz et al., 2004). The coals are of high volatile bituminous C

and B rank. A summary of selected coal quality parameters for these two coal beds in Indiana is given in Table 1, and maps of sulfur content distribution are presented in Figs. 2 and 3.

3. Techniques

Coal seams were described megascopically, and bench samples were collected for moisture, sulfur, ash, heating value, and trace element analysis following ASTM procedures (1985). For all samples, in addition to the raw coal, float fractions at 1.55 g/cm³ were obtained and analyzed.

Trace element concentrations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES) and inductively coupled plasma mass spectroscopy (ICPMS) at the U.S. Geological Survey. USGS procedures for these analyses are outlined in Meier et al. (1996) and Palmer (1997).

Maps generated for sulfur and trace element content utilize all data available from Indiana, including data previously generated and compiled at the Indiana Geological Survey (Hasenmueller and Miller, 1992; Oman et al., 1992; Mastalerz and Harper, 1998; Mastalerz et al., 2004).

4. Results and discussion

4.1. Trace element contents and their lateral variations

Arsenic contents of the Danville and Springfield coals show similar ranges from 0.5 to 43 ppm (whole coal basis) for the Danville Coal and 1 to 50 ppm for the Springfield Coal, with an average of 12.7 ppm for the Danville and 9.4 ppm for the Springfield Coal (Table 1). These averages are close to the world average As content for bituminous coals (9 ppm, Yudovich and Ketris, 2005), significantly lower than average As content for all U.S. coals (24 ppm, Finkelman, 1993)

and higher than 5 ppm average in the Earth's crust (Bouska, 1981). Cadmium concentrations do not exceed 9 ppm, with an average of 0.4 for the Danville and

0.7 ppm for the Springfield coal (Table 1). These values are close to the range of 0.3 to 28 ppm obtained for the Illinois coals studied by Gluskoter and Lindahl (1973)

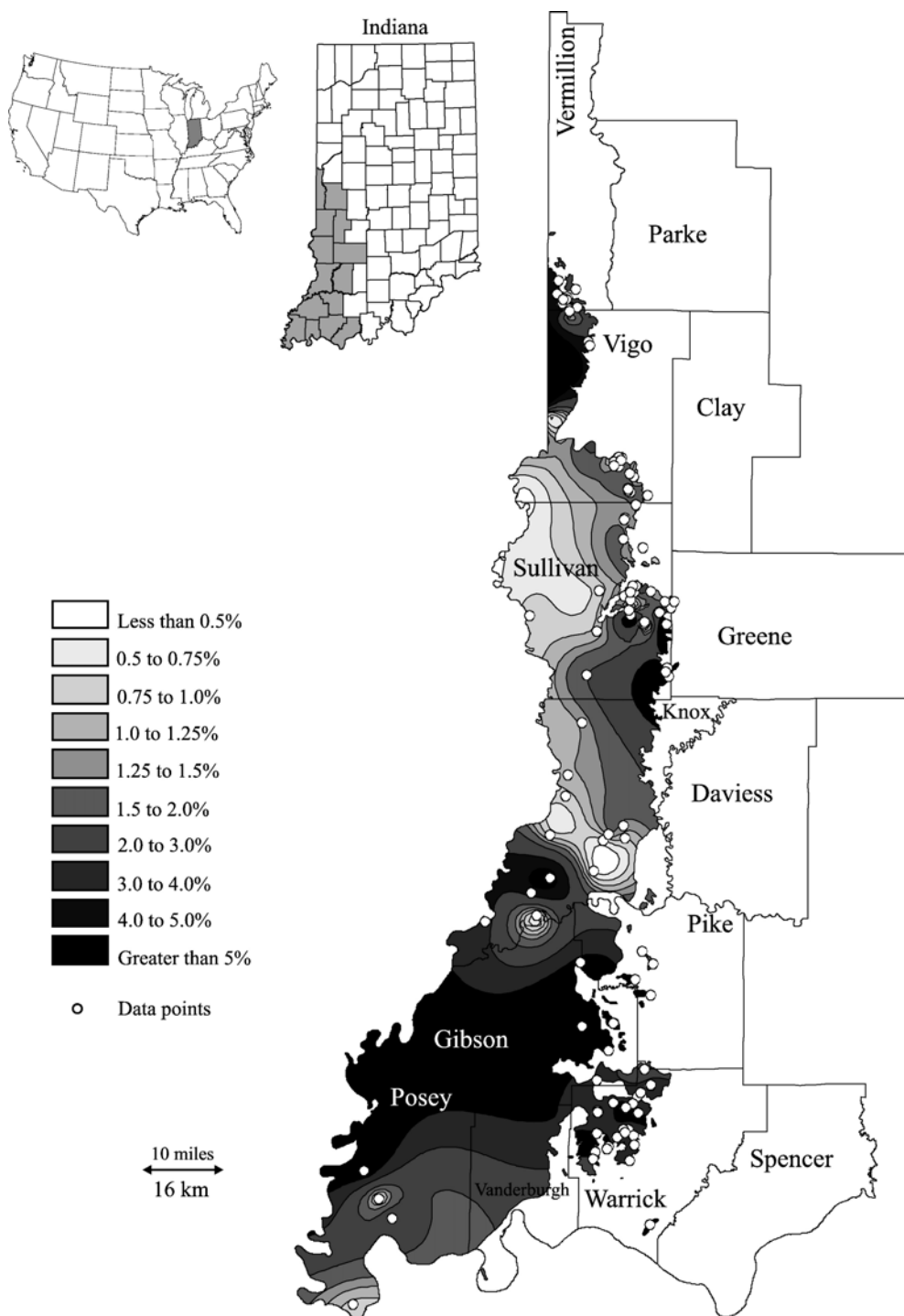


Fig. 2. Map of southwestern Indiana showing sulfur content (wt.%, dry basis) of the Danville Coal Member.

and close to the average for all U.S. coals (0.47 ppm); the average Cd concentration in the Earth's crust is 0.18 ppm (Table 1). Average Pb contents are 21.3 for the Danville coal (higher than U.S. average of 11 ppm, Table 1) and 6.3 ppm for the Springfield. The Zn contents are 101 and 54 ppm for the Danville and the Springfield, respectively, both higher than average (53 ppm) for U.S. coals.

In general for both coal beds, As contents are lowest in parts of Gibson, Knox, Sullivan and Warrick counties, and highest in Posey and Vigo counties for the Danville (Figs. 4 and 5). There is some overlap between the areas of highest As and the areas of high S content and the areas of low As with the areas of low S content (Figs. 2 and 3), but this comparison is difficult because there are far fewer data available for As than for sulfur.

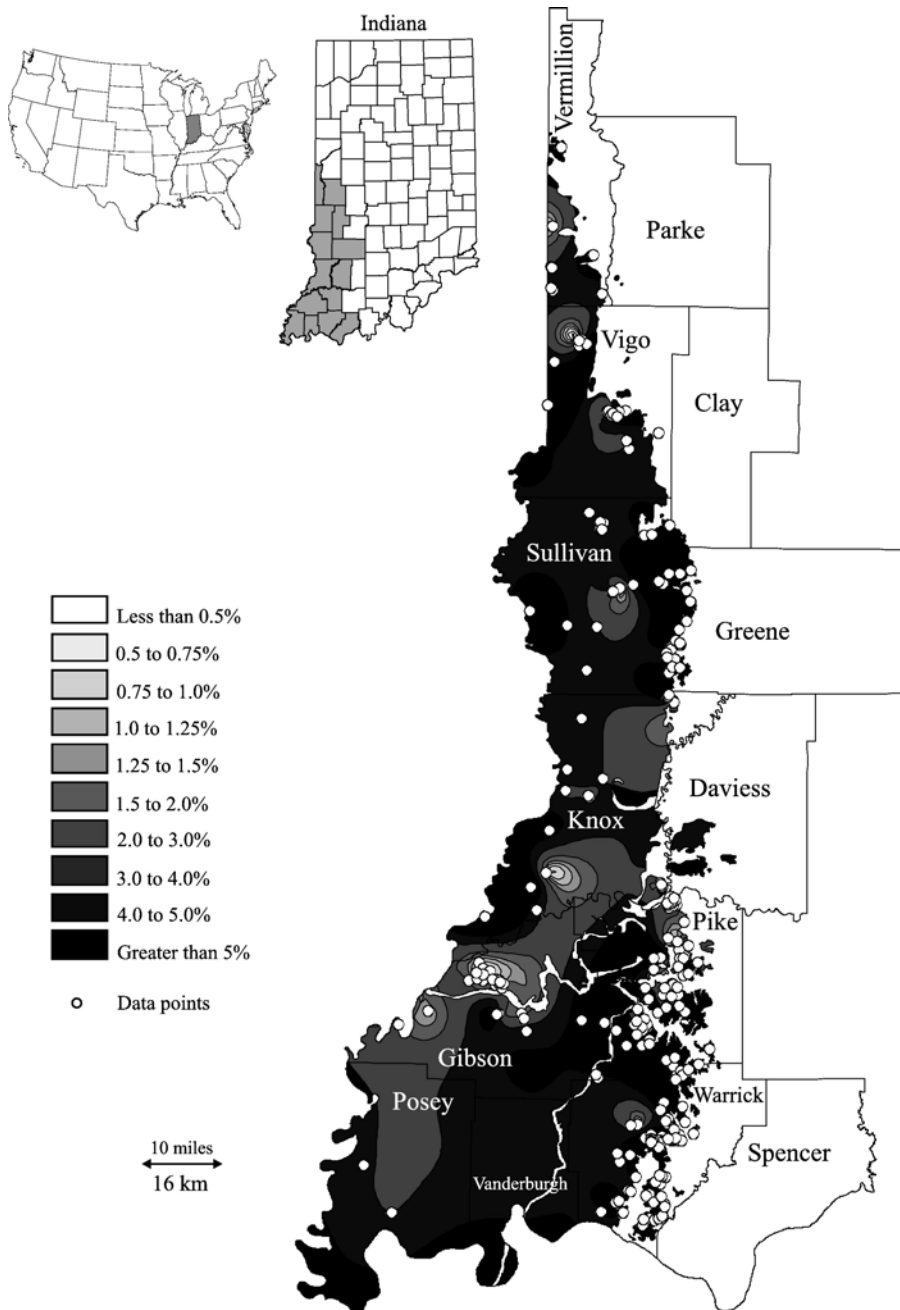


Fig. 3. Map of southwestern Indiana showing sulfur content (wt.%, dry basis) of the Springfield Coal Member.

Distributions of Cd, Pb, and Zn of the Danville Coal are presented in Figs. 6, 7, and 8, and those for the Springfield Coal in Figs. 9, 10, and 11. Because of the limited number of data points, no isolines were generated; rather, the data were divided into two categories, higher and lower concentrations.

4.2. Vertical in-seam variations

The availability of analyses for coal benches from several locations allows us to document vertical changes with coal beds. These changes are discussed from three locations for the Danville Coal, one in Knox County

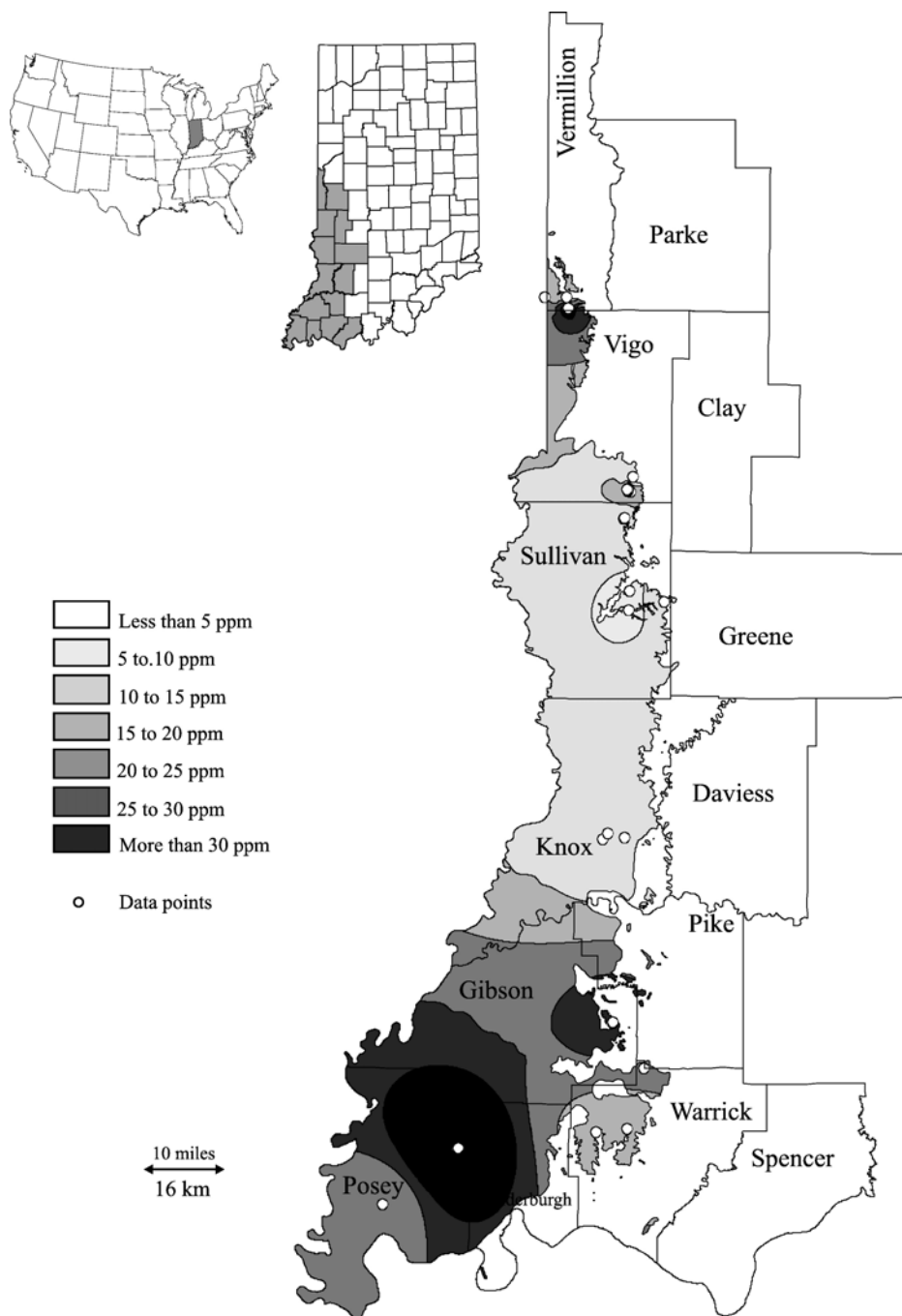


Fig. 4. Map of southwestern Indiana showing arsenic content (ppm, whole coal) of the Danville Coal Member.

(AQ) and two in Sullivan County (F1 and F2), and two locations for the Springfield Coal, one in Gibson County (S) and one in Warrick County (CC) (Table 2). The locations represent active coal mines with significant coal production, and thus, the samples are roughly representative of the Danville and Springfield being currently mined in Indiana.

Cd and Zn generally follow the same trend in vertical seam sections, suggesting they are hosted by the same mineral, most probably sphalerite (ZnS). In the Danville Coal, in one section from Knox (Fig. 12) and two sections from Sullivan County (Figs. 13 and 14), Cd and Zn behave, with few exceptions, in a similar manner (Figs. 12, 13, and 14D,F), following neither pyritic sulfur nor

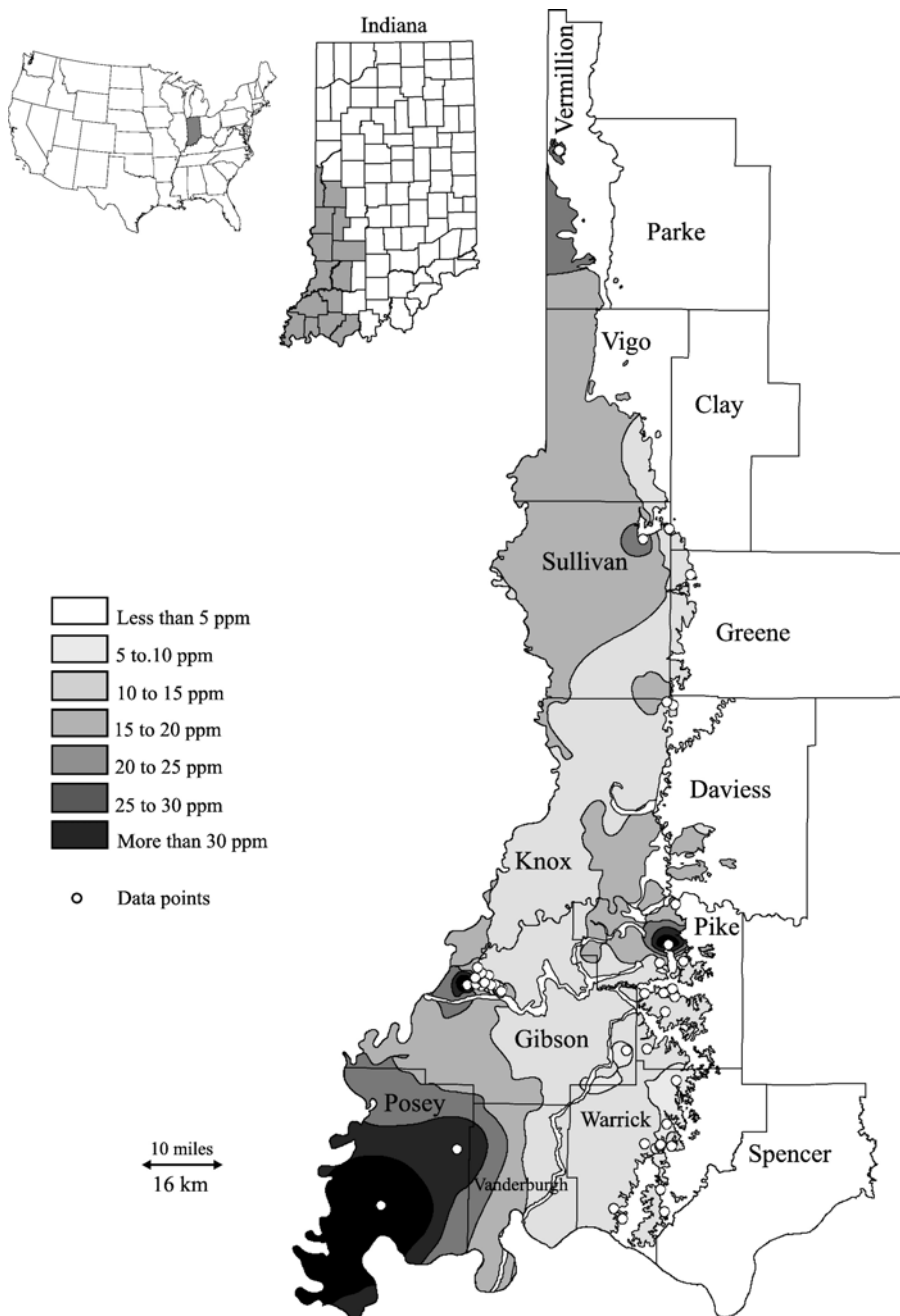


Fig. 5. Map of southwestern Indiana showing arsenic content (ppm, whole coal) of the Springfield Coal Member.

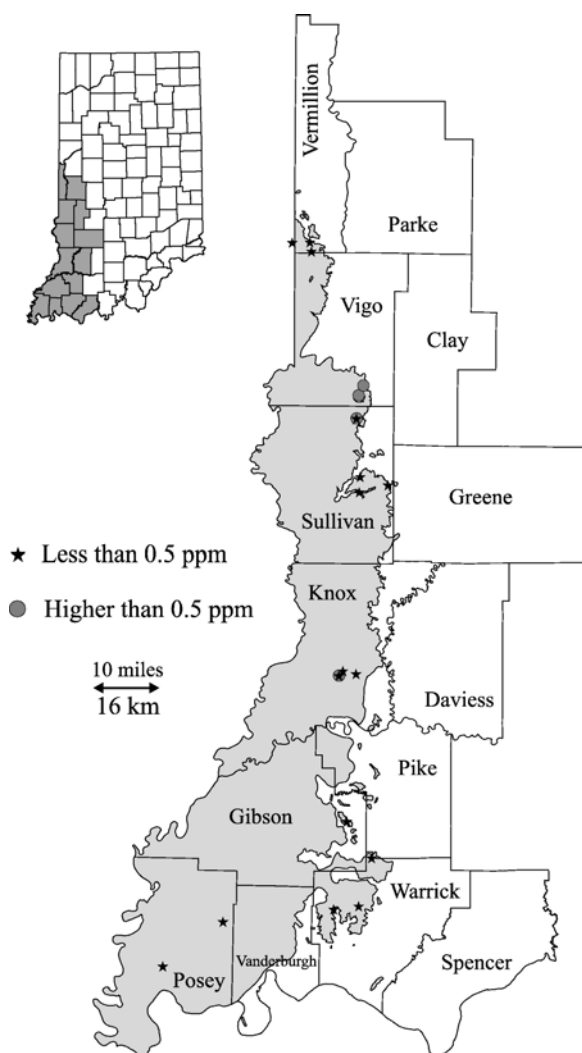


Fig. 6. Map of southwestern Indiana showing cadmium content (ppm, whole coal) of the Danville Coal Member.

ash yield trends (Figs. 12, 13, and 14A,B). Cd and Zn do not correlate with any of the major oxides in the ash (Table 2). Their distribution in the Danville Coal is, however, site specific. In Knox County, the bottom part of the coal has the lowest Cd and Zn concentrations, and the highest level occurs in the middle part of the coal bed (location AQ, Fig. 12, Table 2). In Sullivan County, the study locations (F1 and F2, Table 2) occur within less than 1 km of one another, yet the distributions of Zn and Cd in a vertical seam section are different between locations. In location F1, the top and the bottom benches have the greatest Cd and Zn contents (Fig. 13 D,F); these benches experience high reduction upon washing. At the other Sullivan County location (F2), Cd and Zn contents are lowest in the top bench of the coal (Fig. 14 D,F). These differences in

Cd and Zn distribution in such a close proximity may be related to the influence of varying clastic environments following peat deposition. Indeed, changes from fine-grained freshwater sediments to coarse-grained marine sediments of the overlying Busseron Sandstone Member are frequent in the vicinity of this mine (Mastalerz and Padgett, 2002). Perhaps the more porous lithologies favored migration of Cd- and Zn-rich fluids, causing Cd and Zn enrichment in the uppermost bench of F1 location. This bench has significantly higher contents of CaO, but low, compared to other benches, Fe_2O_3 (Table 2), pointing to early stages of diagenetic calcite precipitation from low-Fe fluids (Kolker and Chou, 1994) that were the likely source for Cd and Zn.

In the Springfield Coal, Cd and Zn distributions are also site-specific: in location CC, their concentration is

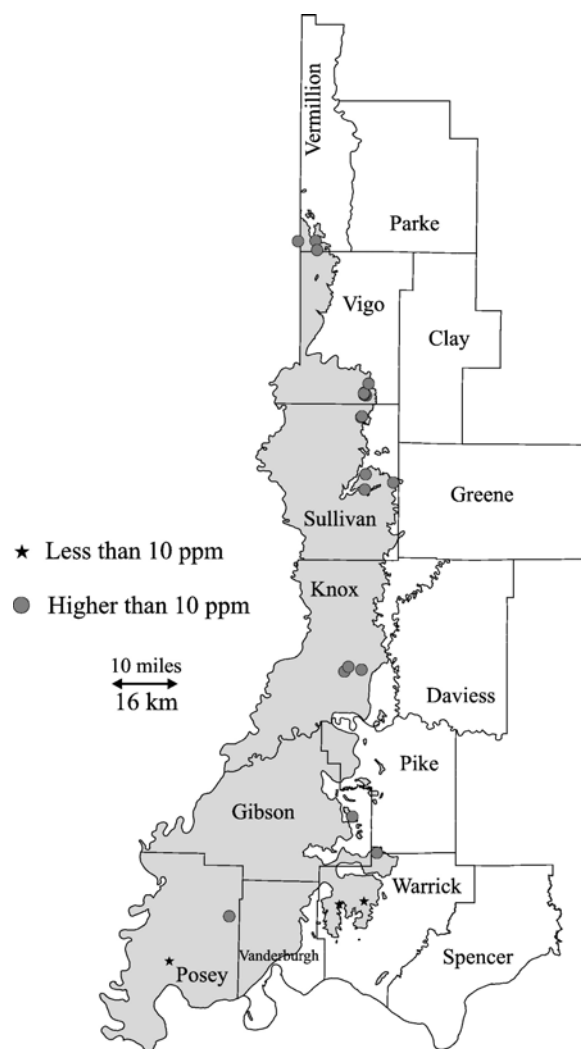


Fig. 7. Map of southwestern Indiana showing lead content (ppm, whole coal) of the Danville Coal Member.

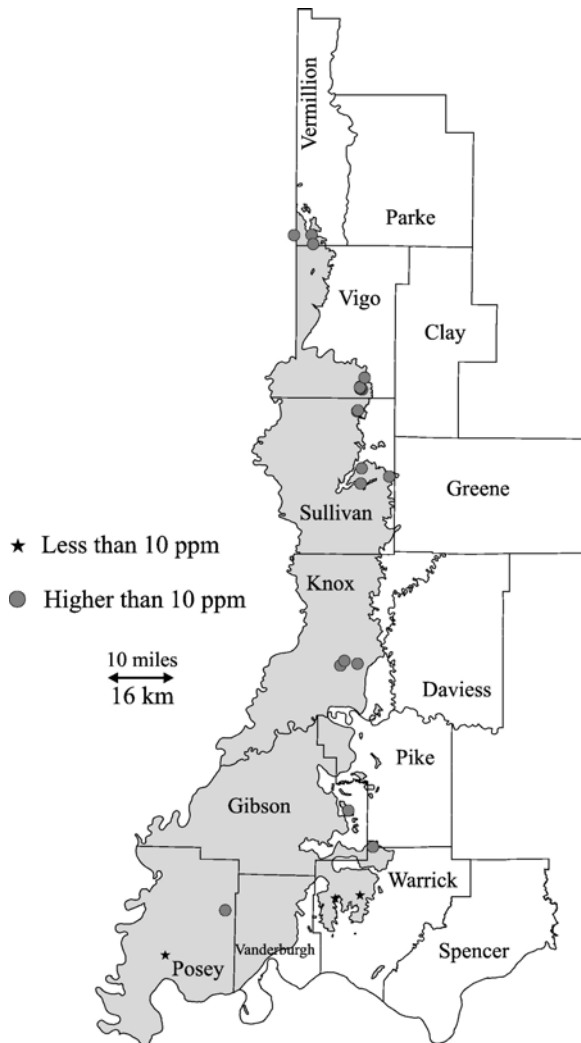


Fig. 8. Map of southwestern Indiana showing zinc content (ppm, whole coal) of the Danville Coal Member.

higher in the lower part of the bed (Fig. 15D,F), and in location S, in the upper part of the coal bed (Fig. 16D,F). Similar to the Danville Coal, no correlation between Cd and Zn and ash and pyritic sulfur has been found (Figs. 15 and 16A,B).

The close correlation between Cd and Zn is not unexpected and has been demonstrated earlier both from the Illinois Basin (Gluskoter and Lindahl, 1973) and other regions in the U.S. based on the data from USGS database (Finkelman, 1994). Cadmium is thought to substitute for Zn in sphalerite (Gluskoter and Lindahl, 1973). In the coals studied, these elements are not associated with pyritic sulfur content or ash yield, yet they are dramatically reduced in the float fraction as a result of washing. These observations suggest that Cd

and Zn are hosted by a high specific gravity mineral, likely sphalerite. Easy removal of these two elements upon cleaning indicates that the parent mineral occurs in large crystals that fill cleats and fractures which, in turn, suggests their late epigenetic origin. Gluskoter and Lindahl (1973) documented sphalerite filling cleats in the Springfield Coal of Illinois.

Arsenic in the Danville Coal in the Knox County section (Fig. 12C) correlates with pyritic sulfur and ash yield, suggesting an association with pyrite, possibly related to the enrichment in SO_4 from overlying sediments, as supported by the greatest As contents at the top of the coal (Fig. 12C, Table 1—location AQ). In Sullivan County, As correlates with ash yield in location F2 (Fig. 14C). In location F1, As content (Fig.

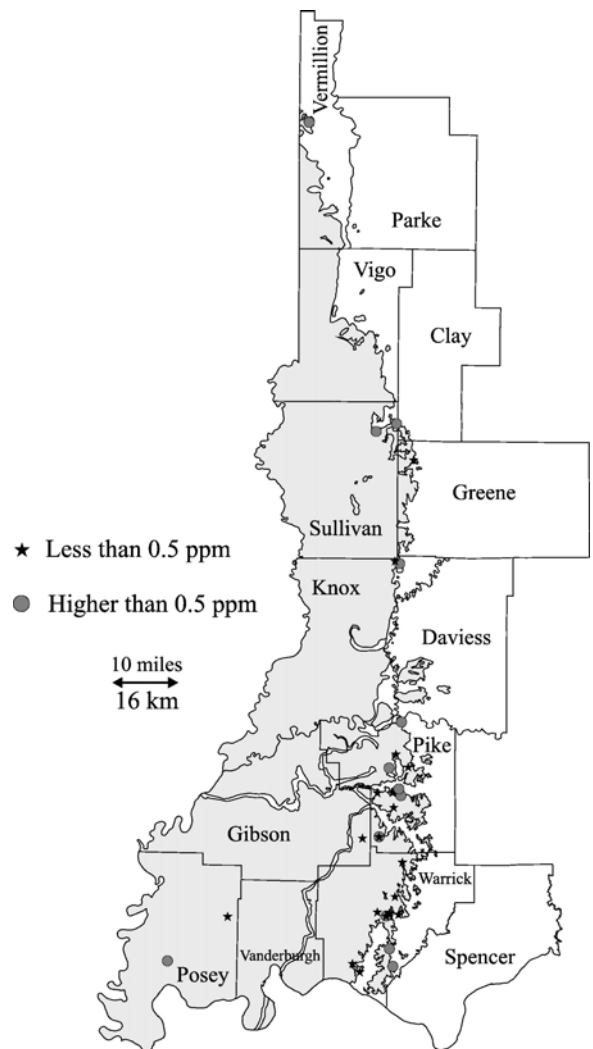


Fig. 9. Map of southwestern Indiana showing cadmium content (ppm, whole coal) of the Springfield Coal Member.

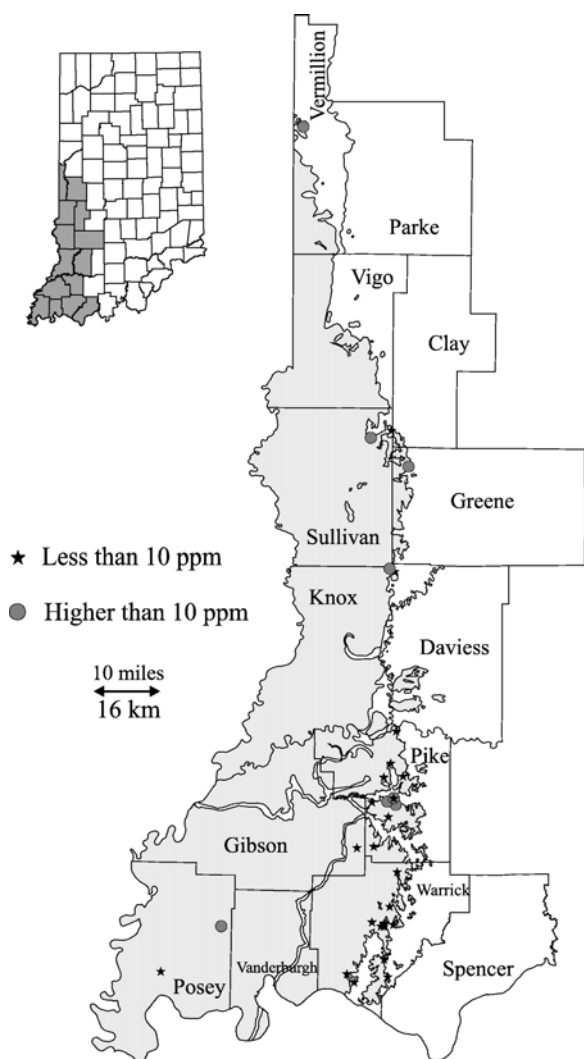


Fig. 10. Map of southwestern Indiana showing lead content (ppm, whole coal) of the Springfield Coal Member.

13C) does not correlate with pyritic sulfur or ash (Fig. 13A,B). In the Springfield Coal, As (Figs. 15C and 16C), in general, follows pyritic sulfur. There is no regularity with regard to As behavior adjacent to the roof or floor lithologies; its maximum concentrations can occur at the top of the coal, in its middle portion, or at the bottom.

Based on these observations, we suggest that As has multiple origins in the coals studied. A relationship between As and pyritic sulfur for the Springfield Coal and for the Danville coal in Knox County suggests that it is associated with pyrite there. Association with pyrite, especially with a late-fracture-filling variety, has been documented in numerous other coals (Minkin et al.,

1984; Dubansky et al., 1988). In our study, As is significantly reduced during washing of the Springfield coal which supports a late cleat-filling pyrite that is easily removed by washing. For the Danville Coal in Knox County, however, As content is not significantly reduced during washing despite a strong relationship with pyritic sulfur (Fig. 12). We suggest that, in this location, As is hosted by early-stage, very-fine-grained pyrite. Such a syngenetic origin of As has been documented from other basins (Dubansky et al., 1988; Ruppert et al., 1992). For the Danville Coal in Sullivan County, the lack of a relationship with pyritic sulfur, the lack of a relationship with any major oxides (Table 2), and only a very modest reduction in As in the float fractions suggest an association with organic matter.

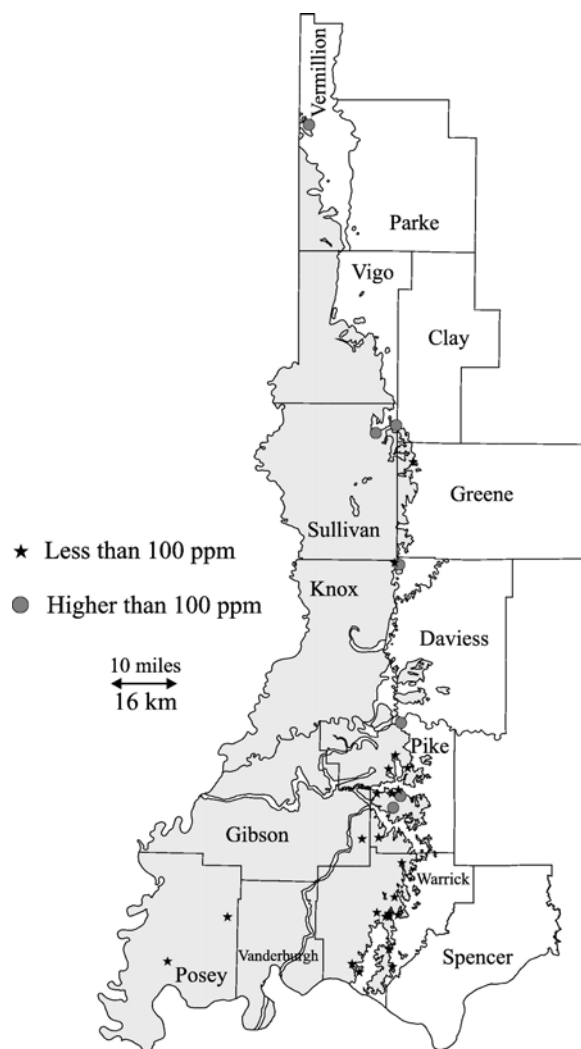


Fig. 11. Map of southwestern Indiana showing zinc content (ppm, whole coal) of the Springfield Coal Member.

Table 2
Ash yield, total sulfur (S_{tot}), pyritic sulfur (S-pyr), Zn, As, Pb, Cd (whole coal basis), and ash composition of coal benches from five locations in Indiana

Location	County	Seam	Benches [cm]	Ash dry	S-pyr dry	S _{tot} dry	ppm			Ash composition (wt.%)										
							Zn	As	Pb	Cd	Na ₂ O	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	P ₂ O ₅	SiO ₂	SO ₃	TiO ₂
AQ	Knox	Danville	0–15	20.05	0.42	0.82	136.70	10.67	25.70	1.28	1.4	20.4	0.63	6.7	3.6	1.8	0.11	64.2	0.93	1.4
			15–43	13.25	0.13	0.59	292.80	1.82	15.90	2.6	1	25.3	1.1	4.5	3.4	1.5	0.08	63.2	1.1	1.4
			43–103	6.26	0.08	0.63	147.10	0.01	10.10	2.79	0.91	24.5	6.3	4.2	3.1	1.3	0.05	51.3	1.6	1.1
			103–148	8.28	0.10	0.53	11.40	0.02	11.50	0.04	0.88	23.5	3.1	9.3	2.9	1.6	0.14	51	1.5	1.2
F1	Sullivan	Danville	0–33	4.49	0.54	1.49	170.60	6.47	14.50	0.75	0.22	15.2	8.3	11.4	1.9	0.55	0.07	30	1.4	0.79
			33–69	11.90	0.51	1.46	14.90	4.43	16.30	0.04	0.26	15.1	1.4	6	2.9	0.72	0.04	38.1	0.78	0.82
			69–96	13.88	0.65	1.50	15.50	4.40	32.60	0.04	0.28	23.6	0.67	10.2	3.3	1.3	0.04	55.1	0.56	1.2
			96–117	8.45	0.55	1.59	122.50	3.19	5.70	0.29	0.27	18.6	0.63	9.8	2.9	1	0.06	42.5	1.1	0.98
F2	Sullivan	Danville	0–34	5.17	0.51	1.35	15.10	4.66	9.10	0.05	0.34	23.4	3.7	15.1	2.4	0.88	0.06	47.3	1.7	1.2
			34–70	12.84	0.70	1.45	49.40	21.31	12.00	0.3	0.32	24.5	1.7	9.9	3	1.3	0.05	55.2	1.3	1.2
			70–93	9.08	0.73	1.52	131.70	5.46	16.80	0.18	0.31	24.6	0.75	12.5	2.9	1.4	0.07	54.7	1.1	1.2
			0–31	12.17	3.15	5.26	12.90	8.51	2.20	0.15	0.42	12.7	7.8	30.4	1.8	0.72	0.06	29.9	5.2	0.65
CC	Warrick	Springfield	31–40	12.65	0.50	2.94	11.90	1.86	3.70	0.11	0.58	20.1	8.7	7.1	2.2	0.85	0.05	45.7	3	1
			43–83	11.90	3.14	6.18	14.80	15.47	3.50	0.13	0.44	11.9	6.2	51	0.97	0.35	0.08	20.3	3.2	0.54
			83–114	13.97	3.89	6.85	149.50	14.95	4.70	1.05	0.4	11.9	1.3	49.8	1.6	0.52	0.08	23.3	0.8	0.55
			114–152	13.74	1.59	4.29	57.70	5.29	3.70	0.25	0.63	19.8	1.5	15.8	2.9	1.1	0.08	46.9	1	1.1
S	Gibson	Springfield	0–33	12.70	3.38	5.64	30.10	8.85	6.32	0.11	0.5	17.6	2.4	27.5	2.6	0.82	0.1	35	2.1	1.1
			33–74	5.78	0.93	3.11	37.60	2.50	10.25	0.2	0.73	22.9	4.8	19.6	2.4	0.76	0.07	36.8	1.6	1.1
			74–103	12.40	5.93	7.25	10.80	3.76	2.83	0.1	0.35	12.9	1.8	43.4	1.6	0.46	0.11	28.6	1.4	0.65
			103–143	11.27	1.56	4.14	13.90	6.15	6.39	0.14	0.68	18	3.8	16.2	3	1	0.07	43.3	1.5	0.94

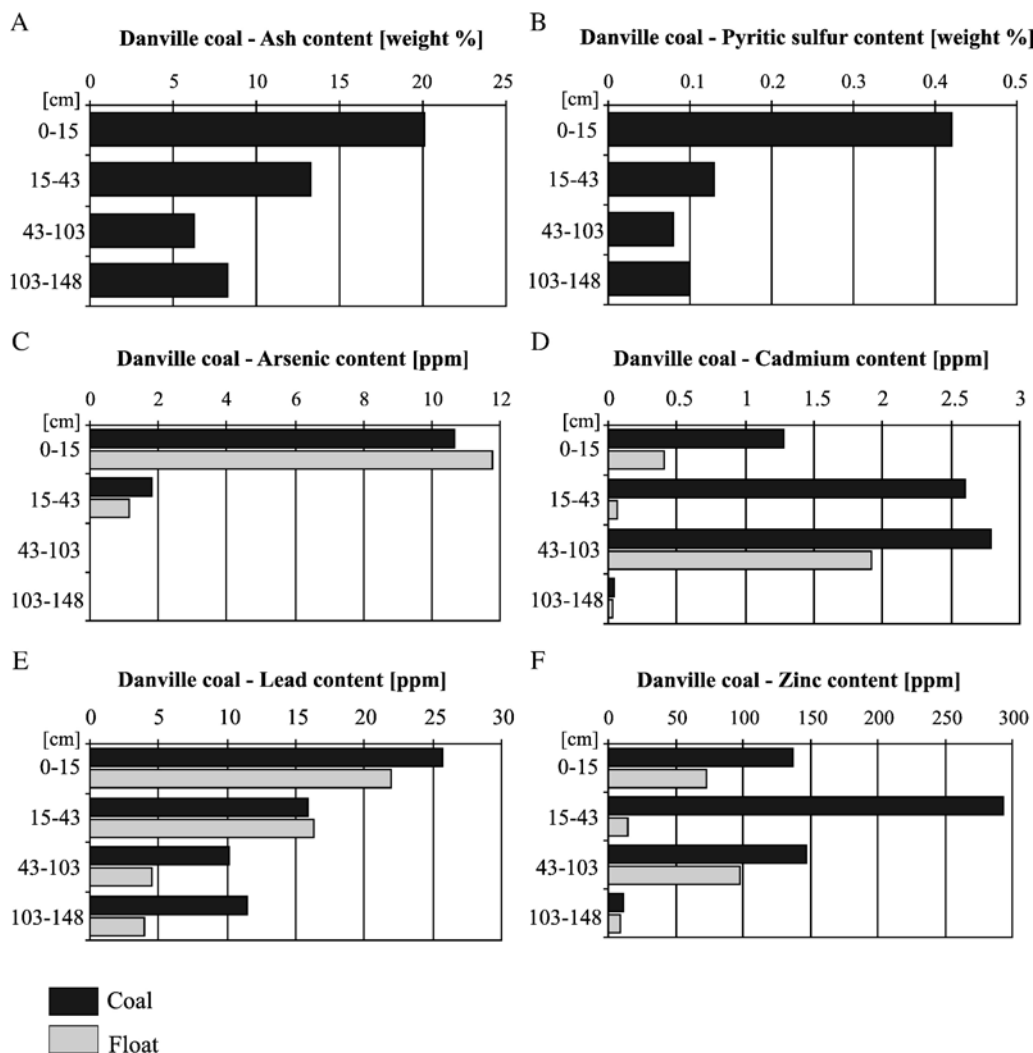


Fig. 12. Diagrams showing coal quality and trace elements content of the Danville Coal member, Knox County, location AQ. A. ash content (wt.%, dry basis), B. pyritic sulfur content (wt.%), C. arsenic content (ppm, whole coal basis), D. cadmium content (ppm, whole coal basis), E. lead content (ppm, whole coal basis), F. zinc content (ppm, whole coal basis).

Lead generally correlates with pyritic sulfur in all locations in the Danville Coal (Figs. 12E, 13E, and 14E), suggesting an association with pyrite or sulfide phases in general (Finkelman, 1994). A very modest reduction of Pb in the float fraction further suggests that the Pb-hosting sulfide was not removed during washing, probably because of its very dispersed nature, as often documented for syngenetic framboidal pyrite.

In the Springfield Coal, however, Pb follows ash yield trends (Figs. 15E and 16E), whereas the relationships with pyritic sulfur and ash are complex. In Warrick County, the bench containing the highest amounts of pyritic sulfur also contains the greatest amount of Pb (Fig. 15B,E) and Pb seems to somewhat

follow pyritic sulfur trends, except in the uppermost bench where high pyrite content corresponds to lower Pb. This uppermost bench does not show reduction in Pb in the float fraction compared to the raw coal (Fig. 15E), suggesting that Pb was not removed during washing. This lack of Pb reduction as a result of washing suggests that Pb might occur as very small crystals of galena or lead selenide (PbSe) in the organic matrix. A similar association is also suggested in the Springfield Coal of Gibson County because Pb does not correlate with pyritic sulfur or ash, and there is no reduction in Pb in the float fraction (Fig. 16). In fact, it appears that most of Pb in the coal beds studied is associated with those minute crystals of pyrite, galena

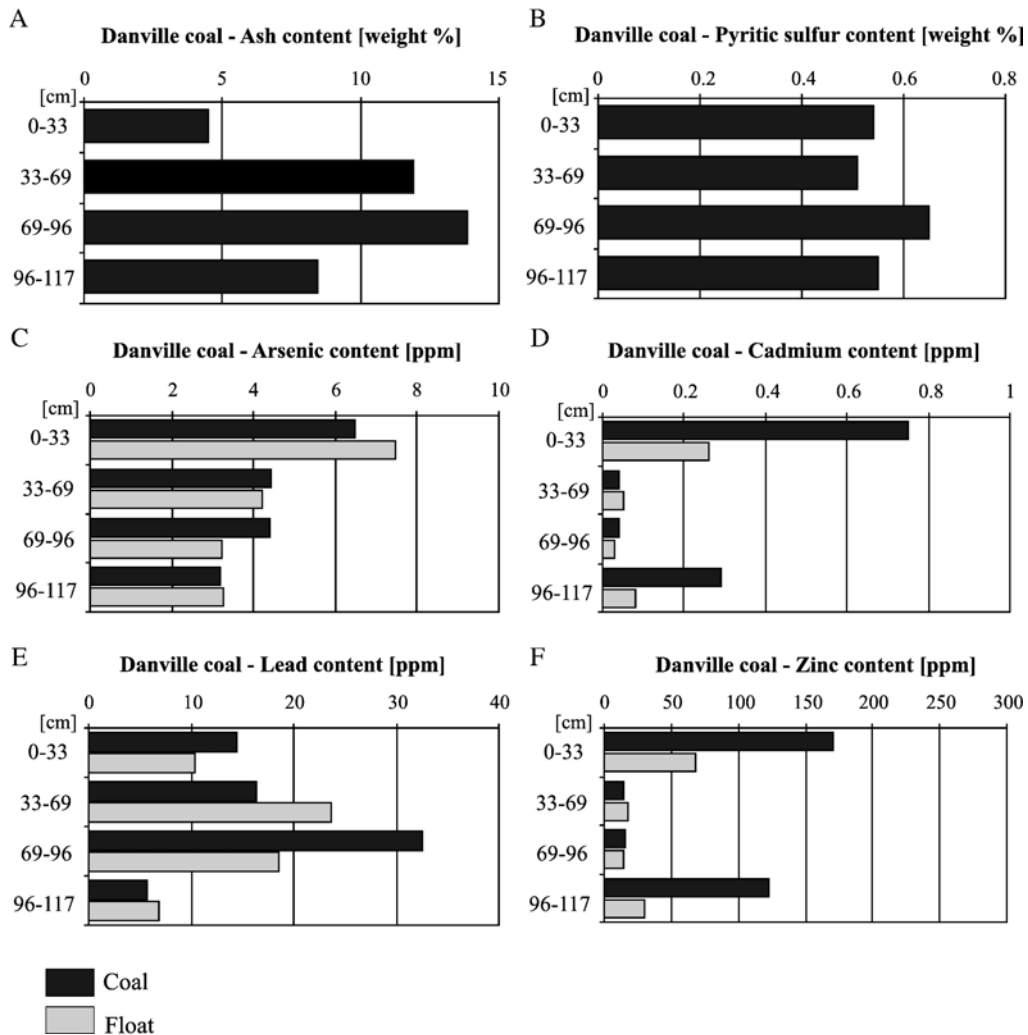


Fig. 13. Diagrams showing Danville Coal Member quality and trace elements content, Sullivan County, location F1. A. ash content (wt.%, dry basis), B. pyritic sulfur content (wt.%), C. arsenic content (ppm, whole coal basis), D. cadmium content (ppm, whole coal basis), E. lead content (ppm, whole coal basis), F. zinc content (ppm, whole coal basis).

or PbSe, as suggested by a generally low average of Pb reduction upon washing (Table 3).

4.3. Raw versus washed coal

Our recent studies in Indiana demonstrate that concentrations of all the elements studied are lowered as a result of conventional coal washing (Mastalerz et al., 2004). On average, As is reduced 47%, Cd 34%, Pb 27%, and Zn 32% in the float fraction compared to the raw coal samples. Reduction of these elements in the whole-seam channel samples of the Danville and the Springfield Coals is shown in Table 3. The degree of reduction varies between the coal beds, Pb content is reduced the least for both coal beds.

Comparing trace elements concentrations in raw coal bench samples to their corresponding float fractions reveals wide variations (Figs. 12–16C,D,E,F), some float fractions are significantly reduced and others are being enriched in trace elements. For example, in the Springfield Coal As is reduced dramatically in high As benches (Figs. 15C and 16C). However, in the Danville Coal, only one out of three benches having relatively high As contents (>5 ppm) behaves this way (Fig. 14C). Cadmium and Zn in float fractions (Figs. 12–16D,F) show generally, with few exceptions, large reductions only in the benches that have Cd content greater than 0.1 ppm, and Zn content greater than 20 ppm. Benches that have lower Cd and Zn contents show little to no reductions. Lead shows rather erratic behavior showing

either reduction or enrichment in the float fractions (Figs. 12–16E). However, in the benches that have high Pb contents (>20 ppm) washing can significantly lower the Pb content of the coal.

The wide range of behavior of the elements we examined indicates different modes of occurrences and also different stages (timing) of mineral emplacement. As discussed earlier, elements emplaced epigenetically, residing in the geochemical phases filling cleats and fractures, will be easily removed from coal during washing, whereas those early emplaced and finely dispersed in coal will not be removed during conventional washing.

5. Conclusions

1. Ranges of As, Cd, Pb, and Zn contents in the Danville and Springfield Coals in Indiana are typical of other Pennsylvanian coals. These elements, except Pb, experience significant, though variable, reduction during coal washing; Pb is reduced only slightly.
2. Zn and Cd behave in the same manner in the coals owing to their common association with sphalerite. Arsenic is mainly associated with pyrite, both syngenetic or epigenetic. Lead appears to be associated with minute crystals of galena or PbSe that stay in the float fraction during washing.

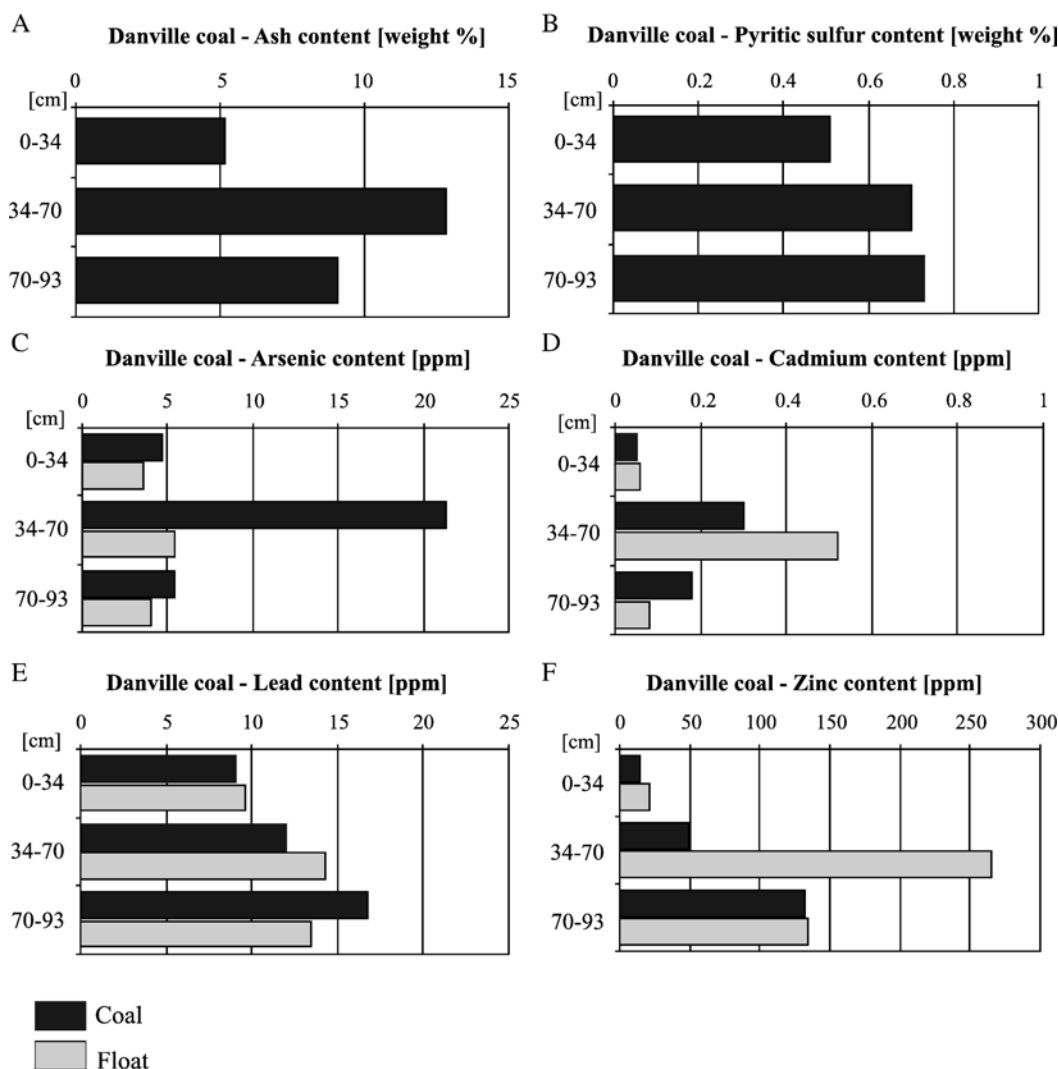


Fig. 14. Diagrams showing quality and trace elements content of the Danville Coal Member, Sullivan County, location F2. A. ash content (wt.%, dry basis), B. pyritic sulfur content (wt.%), C. arsenic content (ppm, whole coal basis), D. cadmium content (ppm, whole coal basis), E. lead content (ppm, whole coal basis), F. zinc content (ppm, whole coal basis).

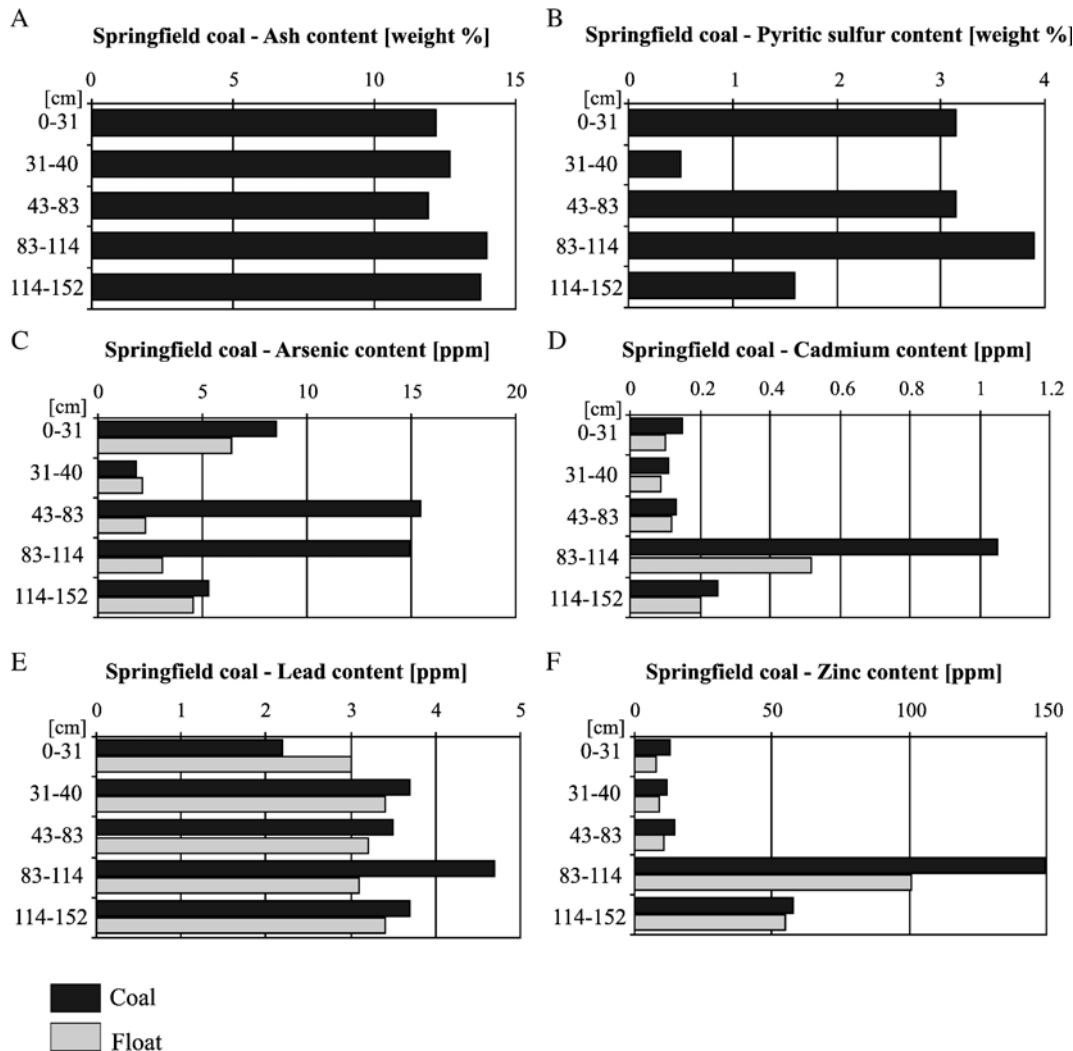


Fig. 15. Diagrams showing quality and trace elements content of the Springfield Coal Member, Warrick County, location CC. A. ash content (wt%, dry basis), B. pyritic sulfur content (wt%), C. arsenic content (ppm, whole coal basis), D. cadmium content (ppm, whole coal basis), E. lead content (ppm, whole coal basis), F. zinc content (ppm, whole coal basis).

3. Relatively high values of all the elements studied are generally related to post-depositional diagenetic enrichment.

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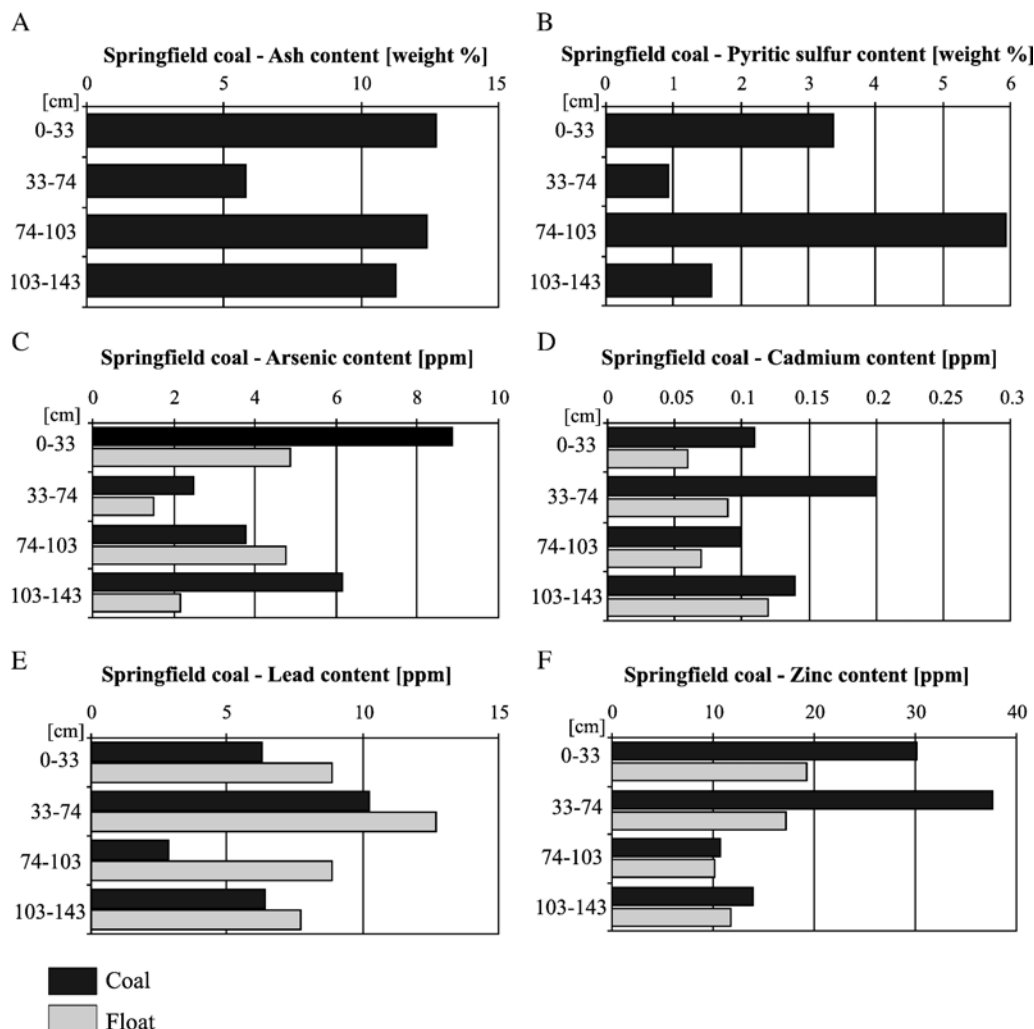


Fig. 16. Diagrams showing quality and trace elements content of the Springfield Coal Member, Gibson County, location S. A. ash content (wt.%, dry basis), B. pyritic sulfur content (wt.%, dry basis), C. arsenic content (ppm, whole coal basis), D. cadmium content (ppm, whole coal basis), E. lead content (ppm, whole coal basis), F. zinc content (ppm, whole coal basis).

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Table 3

Comparison of As, Cd, Pb, and Zn contents in raw coal and corresponding float fractions for the Danville and Springfield Coal Members

Units	Whole coal	Float fraction	% Reduction
<i>Danville</i>			
As (ppm, whole coal)	5.79	4.43	23
Cd (ppm, whole coal)	0.95	0.5	47
Pb (ppm, whole coal)	15.44	12.79	17
Zn (ppm, whole coal)	111	81	27
<i>Springfield</i>			
As (ppm, whole coal)	7.36	3.3	55
Cd (ppm, whole coal)	0.26	0.17	35
Pb (ppm, whole coal)	3.18	3.03	5
Zn (ppm, whole coal)	40	29	28

Data from Mastalerz et al., 2004.

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