SOURCE AND DISTRIBUTION OF PHOSPHORUS

IN BRITISH COLUMBIA COAL SEAMS

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INTRODUCTION

Phosphorus contents of coal from around the world vary although there is a tendency for Permian coals from India and Australia, and Cretaceous coals from Western Canada to have more phosphorus than Carboniferous coals from Europe and USA (Table 1). This may be because of the evolution of vegetation type over geological time or because of the conditions in the coal swamps. Data presented here suggest that most of the phosphorus in coal derives from the original vegetation and, in fact, the amount of phosphorus in coal may be less than expected based on its concentration in vegetation. How the phosphorus is removed from the coal is less clear although a number of possible methods are suggested that infer broad distribution patterns of phosphorus in various lithotypes and macerals. In some cases there is evidence to indicate that phosphorus is concentrated in the inert macerals, but in other cases the evidence is contradictory or ambiguous.

Phosphorus is generally considered an undesirable element in steel, which it makes brittle. It can be removed from the hot metal used to make the steel, but companies generally prefer to control the amount entering the steel-making process. Phosphorus originates in the iron ore, sinter pellets and in the coal used to make blast furnace coke. Steel mills have limited sources of supply of iron ore but can buy coal from a number of suppliers. They therefore sometimes give preference to coals with lower phosphorus contents, and the phosphorus content can have implications on the marketability of coal for coke making. This is generally not the case for thermal coal in which phosphorus contents ranging from 0.1 to 1.5% P_2O_5 in ash may be acceptable (Skorupska, 1993).

Limited data indicate that phosphorus is difficult to remove from coal by conventional washing techniques. It is therefore important, in metallurgical coal mines, to understand the distribution of phosphorus in the coal seams, because blending of the run of mine (ROM) coal, rather than washing, may be the best way of controlling the amount in clean coals.

Data collected during this study are not identified with respect to any particular mine and seams are identified by letter, starting with A at the base of the Mist Mountain Formation. The lettering system does not correspond with the seam numbering in any particular

mine, but does retain the relative statigraphic positions of all the data discussed in this paper. Samples were collected from the Fording, Greenhills, Elkview and Line Creek mines (Figure 1). At some mines incremental channel samples were collected across seams. In addition samples of run-of-mine (ROM) and plant-product coal were collected. Coal samples were analyzed for phosphorus, sulphur, sulphur forms, as well as a number of other properties. Samples of hangingwall and footwall rock, and possible tonstein bands, were also collected and subjected to x-ray diffraction and oxide analysis.
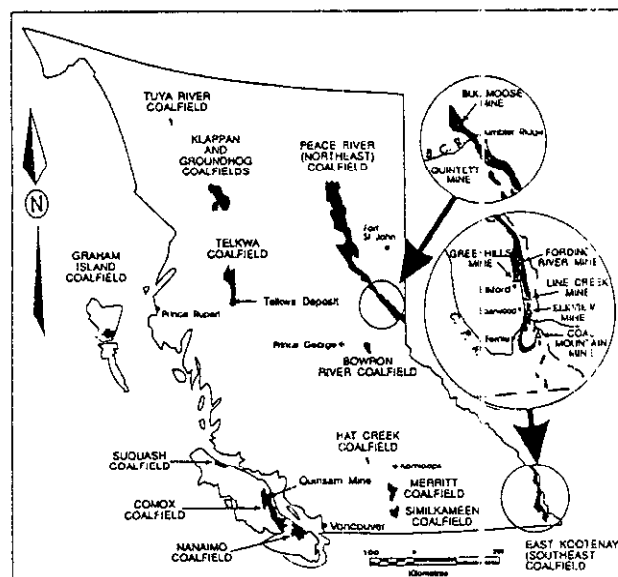

Figure 1. Location map for coal mines and properties in British Columbia.

PREVIOUS WORK

There is abundant literature on major oxides, minor and trace elements in coal. Unfortunately phosphorus is often neglected in these studies, apparently sometimes not being considered either a trace element, important major oxide or minor element. Also, when data are located, it is often not clear if they are for raw or washed samples. Sometimes the data are expressed as P_2O_5 in ash without providing the concentration of ash in the sample, making it impossible to calculate the concentration of phosphorus in the total sample. In short, there is deceptively little useful published phosphorus data.

There have been a number of studies on the occurrence of minor and trace elements in coal, conducted with the goal of classifying the elements into

TABLE 1
PHOSPHORUS CONTENT IN MAJOR COAL BASINS

COAL BASIN	COUNT	P ppm	TYPE	AGE	SOURCE
World	?	500	coal	variable	Valkovic (1983)
USA					
US coals	32	185	coal	variable	Abernathy & Gibson (1963)
Appalachia	754	182	coal	Carboniferous	Finkleman (1980)
Pennsylvania	31	191	coal	Carboniferous	Abernathy et al. (1969)
Illinois	11	260	coal	Carboniferous	Abernathy et al. (1969)
Arkansas	10	8	coal	Carboniferous	Haley (1978)
Washington	6	763	coal	Tertiary	Abernathy et al. (1969)
Britain					
Northumberland, England	33	610(122)*	coal	Carboniferous	Asuen (1987)
Australia					
New South Wales	?	310	coal	Permian	Swaine (1977)
Queensland	11	700	coal	Permian	Queensland Coal Board, (1975)
South Africa					
Whitbank	41	920	coal	Permian	Cairncross et al. (1990)
India	5	5640	coal	Permian	Pareek and Bardhan, (1985)
Japan	13	400	coal	Tertiary	Gmelin (1965)
U.S.S.R.	427	570	peat	Tertiary	Gmelin (1965)
Canada					
Nova Scotia	16	63	coal	Carboniferous	Faurschou et al. (1982)
Saskatchewan	9	226	coal	Tertiary	Faurschou et al. (1982)
British Columbia					
Klappan	16	1020	coal	Cretaceous	Coal Assessment Reports
Gething Formation	?	630	coal	Cretaceous	Grieve (1992)
Gates Formation	?	420	coal	Cretaceous	Grieve (1992)
Mist Mountain Formation	?	760	coal	Cretaceous	Grieve (1992)
Telkwa prospect	66	520	coal	Cretaceous	Matheson et al. (1994)
Quinsam mine	14	128	coal	Cretaceous	Matheson et al. (1994)
Hat Creek prospect	43	176	lignite	Tertiary	Hill (1990)
Tuya River prospect	2	136	lignite	Tertiary	Ryan (1991)
Rapid River prospect	1	65	lignite	Tertiary	unpublished data
Coal River prospect	1	436	peat	Tertiary	unpublished data

* data converted to coal basis. P% (coal) = P%(ash) x ash% / 100 assuming 20% ash

those having organic or inorganic affinity. In the classic sense, organic affinity means that the element is part of the organic molecules that make up the coal. In practice, elements that are difficult to remove by conventional washing methods, and tend to remain with the coal, are described as having an organic affinity. These elements may occur in very small mineral grains dispersed in the coal in a way unrelated to the ash content. Consequently the term organic affinity may be somewhat misleading and a better way of describing the occurrence of elements may be to simply to refer to them as elements that follow the coal or the ash during washing. Those following the coal will be difficult to remove and may be a problem for the coal user. Those removed by washing may provide problems for the coal producer when disposing of the tails and coarse reject material.

A number of papers have investigated the distribution of phosphorus in coal. Two of the key papers are by Finkleman (1980) and Gluskoter et al. (1977). There is no clear agreement in these papers as to whether phosphorus has organic or inorganic affinities and they suggest a number of possible sources for the phosphorus. The comprehensive paper by Gluskoter et al. used washability analysis to assign elements a coal or ash affinity. They found that phosphorus sometimes has an inorganic affinity but in a majority of the cases, follows the coal. Finkleman reviewed existing literature and used x-ray diffraction and scanning electron microscope techniques to identify the modes of occurrence of many elements, including phosphorus, in coal. Powell (1987)

suggested that ionic potential can be used to separate elements in organic or inorganic affinities and that, based on this, P^{3+} should have organic affinity and P^{5+} should be inorganic.

Studies of phosphorus in British Columbia coals include Van Den Bussche and Grieve (1990), Grieve and Holuszko (1991) and Grieve (1992). This paper builds on the work of Grieve (1992).

A number of researchers investigated the distribution of elements, including phosphorus, in seam sections. These include Karner et al. (1986) who studied the distribution of elements in a North Dakota lignite of Paleocene age and described phosphorus as having an uncertain or inorganic association. Other papers include Harris et al. (1981) who studied coals in eastern Tennessee, and Hill (1990) who studied the Hat Creek deposit in British Columbia.

PHOSPHORUS IN STEEL MAKING

Phosphorus can make some grades of steel brittle, in part because it remains as an oxide impurity. Low phosphorus contents are essential in high-quality construction steels, though it is not always harmful and is added to certain steels to improve machineability or fluidity of castings (Stubbles, 1986).

Phosphorus enters the steel from the iron ore, sinter pellets, coke and in the coal used in pulverized coal

injection. Other sources that are sometimes important are recycled sinter from steel making and scrap iron, both of which are added to the blast furnace and concentrate and recycle phosphorus back into the furnace. The phosphorus content of iron ore depends on its origin. Sedimentary hematite ores generally contain less than 0.1% whereas limonite or siderite ores contain up to 1.5%. Magmatic magnetite ores contain the most, ranging up to 2%. Most of the iron ore now mined in the Great Lakes area of North America contains less than 0.05%. The sensitivity of steel mills to phosphorus from sources other than the iron ore depends on the content in the iron ore they use and on what technology they have for removing phosphorus from hot metal. It is generally assumed that all the phosphorus reporting to the blast furnace will end up in the hot metal. Steel mills therefore have two choices, either limit the phosphorus load to the blast furnaces, or remove it from the hot metal later. North American steel mills have limited technology for removing phosphorus and therefore attempt to minimize the load to the blast furnace and attempt to keep the concentration in the hot metal to less than 0.05%. This effectively puts pressure on the coal suppliers to maintain a low concentration of phosphorus in the coal, and some steel mills require concentrations in the coal to be less than 0.03% phosphorus.

In Japan, hot metal is produced with as much as 0.1% phosphorous, but it also has a low silicon content which makes it possible to use various basic fluxes to reduce the phosphorus content of the hot metal to less than 0.01% and sometimes down to 10 ppm. In the U.S., phosphorus contents in the hot metal are kept below 0.05% and less aggressive dephosphorization techniques used to remove it. Stubbles (1986) provides a comprehensive discussion of the sources of phosphorus in steel and different dephosphorization techniques.

It is possible to estimate the contribution that phosphorus from coal makes to the total in the hot metal, because it is all retained in the coke (Mahony et al., 1981). It is therefore possible to calculate the content in the coke by using an estimate of the coke yield, which is often about 78% for western Canadian coals. Coke to hot metal ratios in blast furnaces are dropping with the introduction of pulverized coal injection (PCI) technology. If a coke rate of 350 kilograms per tonne hot metal (THM) is assumed, then it is possible to calculate the amount of phosphorus added from the coke. There is an additional complication in that most geological literature expresses the phosphorus content in coal as percent P_2O_5 in the ash. Figure 2 provides a set of curves that estimate the coal-derived phosphorus in the hot metal given the ash content of the coal and the P_2O_5 content of the ash. The diagram assumes a 78% coke yield, a 350 kg/THM ratio, and that all the phosphorus from the coke enters the hot metal. As an example, a sample with 0.6% P_2O_5 and 9% ash has a phosphorus content in coal of 0.0285% and in the resultant coke of 0.03%. If this phosphorus is added to the hot metal (assuming 350 kg coke/THM) then it will account for 0.0105% phosphorus in the metal. This amount will be added to that already present in the iron ore and the total
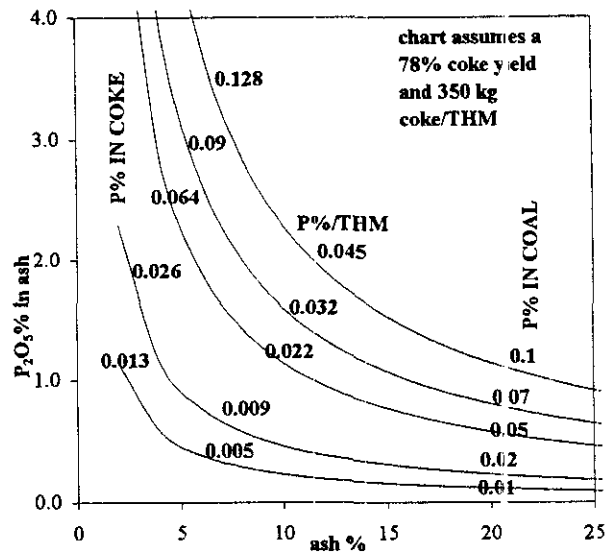

Figure 2. Relationship of P_2O_5% in ash to phosphorus in coal, coke and hot metal.

must not exceed the hot metal concentrations acceptable to the steel mills, which are in the range of 0.03%.

PHOSPHORUS MINERALS FOUND IN COAL

There are a limited number of phosphorus minerals that have been identified in coal; the important ones are described in Table 2. They fall into three major groups: the apatites; the crandallite (plubogummite) group characterized by the presence of aluminum; and the monazites, characterized by the presence of rare earths. Apatite has been reported in a number of western Canadian coals (Grieve, 1992) and is often present as fluorapatite. Apatite averages 17.3% phosphorus and flourapatite contains, on average, 3.5% fluorine. The ratio of fluorine to phosphorus in the apatite can range from 0.0 to 0.2 and for fluorapatite averages about 0.2. This means that a plot of phosphorus versus fluorine cannot be used to identify the presence of fluorapatite unless a slope of 0.2 is derived, especially as fluorine has other possible hosts in coal. Plots of phosphorus versus fluorine data in Grieve (1992) have slopes ranging from 0.4 to 0.86, indicating a considerable excess of fluorine above that required to make fluorapatite. The ratio of P_2O_5 /CaO in apatite is more constant than the F/P ratio and averages 0.755. If the P_2O_5/CaO ratio exceeds this, then it is very unlikely that the phosphorus is present as apatite and it may be truly organic, present in crandallite group minerals, or in monazite.

The crandallite group includes the minerals gorceixite, goyazite and crandallite. Gorceixite is a barium-aluminum phosphate containing, on average, about 10% phosphorus, 20% barium oxide and variable but small amounts of calcium oxide. It is sometimes reported as the phosphorus mineral in coal and has been reported in tonsteins (Grieve, 1983). Strontium is often associated with barium, and the strontium mineral

TABLE 2
PHOSPHORUS MINERAL ANALYSES
from Dana's System of Mineralogy, Palache et al. (1951)

NAME	count	CaO	MnO	P₂O₅	F	Cl	H₂O	CO₂	F/P	P	P₂O₅/CaO
APATITE	15	52.62	0.98	39.48	2.05	0.69	1.18	1.29	0.12	17.23	0.76
formula		Ca₅(PO₄)₂(OH,F,Cl)									
		CaO	Al₂O₃	P₂O₅	BaO	H₂O	CeO	P	Ba/P		
GORCEIXITE	5	1.16	34.54	23.69	19.72	14.40	2.18	10.34	1.68		
formula		Ba,Al₃(PO₄)₂(OH)₅,H₂O									
		SrO	Al₂O₃	P₂O₅	BaO	H₂O	P	Sr/P			
GOYAZITE	4	19.50	37.92	24.84	2.08	14.51	10.84	1.61			
formula		Sr,Al₃(PO₄)₂(OH)₅,H₂O									
		Ce₂O₃	(LaNd)₂O₃		Y₂O₃	ThO₂	Fe₂O₃	P₂O₅	P	Th/P	
MONAZITE	4	28.06	30.57		2.77	8.24	0.70	28.18	12.30	0.63	
formula		(Ce,La,Th)PO₄									

TABLE 3
CORRELATION COEFFICIENTS OF PHOSPHORUS VERSUS OTHER ELEMENTS

REFERENCE	DESCRIPTION	COUNT	Ca	Ba	Sr	F	Th
Gluskoter et al. (1977)	Illinois	114	-0.22	-0.13	0.64	0.38	0.02
Harris et al. (1981)	Eastern Tennesse	20	0.52	ND	0.97	ND	ND
		44	0.22	ND	0.93	ND	ND
Hill (1990)	Hat Creek, B.C.	64	0.17	0.64	0.89	ND	ND
Asuen (1987)	Northumberland, England	33	-.042	ND	-0.128	ND	0.177

equivalent of gorceixite is goyazite. Crandallite is the calcium end-member. High barium and strontium and low fluorine contents in the ash, probably indicate the presence of gorceixite or goyazite rather than apatite. The strontium and barium in gorceixite and goyazite may originate from interstitial waters, vegetation or weathering of carbonates. Initially the barium and strontium were probably adsorbed onto clays or organic material, but during early diagenesis they were incorporated into phosphate minerals. Gluskoter et al. (1977) performed oxide analyses on ashes from a number of coals and produced a correlation matrix which indicates that phosphorus generally has a poor correlation with other elements except for strontium. Harris et al. (1981) also found a good correlation of phosphorus with strontium (Table 3). Their incremental samples indicate a wide variation in phosphorus concentrations, but there is a good correlation with the strontium concentrations of the samples, indicating the possible presence of goyazite. Goyazite, on average, has a Sr/P ratio of 1.61 (Table 2) whereas the two seams studied have Sr/P ratios of 0.405 and 0.27. Unfortunately the authors did not measure barium which, if it had also correlated with phosphorus, would have suggested the presence of gorceixite. The correlation of phosphorus to calcium is poor, indicating it is probably not present as apatite.

Phosphorus concentrations in Carboniferous coals from England (Asuen, 1987), are low, averaging 0.06%, and do not correlate with either calcium or strontium concentrations. The phosphorus may be present as gorceixite or monazite, or may be organically bound. Finkelman (1980) reports that monazite occurs in about 50% of the samples he studied and apatites in about 10%. Brown and Swaine (1964) state that phosphorus usually occurs as fluorapatite in Australian coals.

SOURCES OF PHOSPHORUS IN COALS

Phosphorus in coal originates from four sources; the first three are inorganic and the fourth organic. They are:
As a component of the sediment introduced into the swamp.
As a component of volcanic ash bands (tonstein bands).
As a component of the original vegetation.
From animals or as isolated grains of phosphorus-rich minerals derived from volcanic activity or basement erosion and introduced separately from normal ash material.
After coalification, the phosphorus may be present:
Bound to the coal structure.
As very small disseminated phosphatic mineral grains in the microporosity of the coal.
As a component of ash or tonstein bands.
As coatings on cleat surfaces.
As occasional detrital fragments of phosphorus-rich minerals of extraneous origin.
Figure 3 illustrates the possible inter-relationships between source and location of phosphorus in coal after diagenesis has permitted mobility and recrystallization. The figure also indicates relative ease of removal and whether the amount of phosphorus is likely to correlate with ash, reactive macerals or inert macerals in the coal.
A sediment source implies a correlation with the amount of ash in the seam and an underlying control which relates back to the basement rocks for the coal-bearing stratigraphy. Any phosphorus-rich grains in the ash must be very small so that they are completely mixed with the ash material and are introduced into the swamp in a constant proportion with the ash. If the phosphorus is introduced as a component of tonstein bands, then the coal adjacent to them may also be high in phosphorus. It
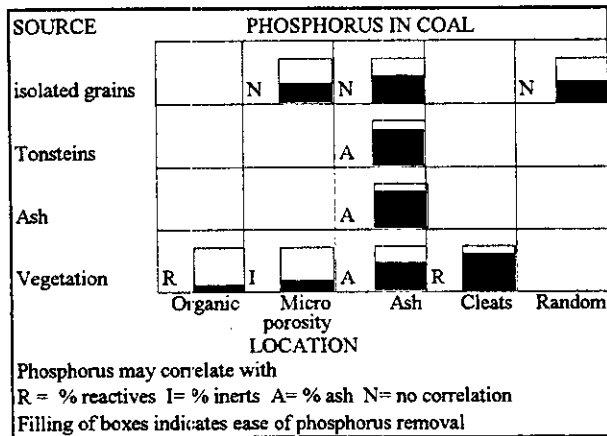
Figure 3. Source *versus* location of phosphorus in coal.

does not seem reasonable that a thin tonstein band can have a marked effect on the phosphorus content of a coal seam 1 to 5 metres thick. Phosphorus introduced as isolated grains will not correlate with either the ash or coal content of the seam. Phosphorus minerals generally have densities 20% to 50% greater than common ash-forming minerals. It is therefore possible to visualize different methods of introducing them into the swamp. The vegetation source may be the most important and it implies a relationship of phosphorus content to the total amount of organic material and probably some sort of underlying maceral control.

In general, it may not be realistic to attempt to distinguish between an extraneous or organic source for the phosphorus by the washing characteristics of the coal or by whether it is now present as identifiable phosphorus minerals.

SEDIMENT SOURCE

The sediment transported into the coal swamp can best be described as a shale and it is therefore important to investigate the phosphorus contents of shales. Wedepohl (1978, Table 15-K-1) provide phosphorus data from a number of sources. The table lists average P_2O_5 contents of a variety of rocks and the data for shale are reproduced here in Table 4. The data are remarkably

consistent and average 0.15% P_2O_5 (or 0.065% P). A number of other papers quote oxide analyses for shales that include P_2O_5 contents and average values range from 0.07% (Turekian and Wedepohl, 1961) to 0 18% (Blatt *et al.*, 1980) and 0.26% (Huang, 1962). The data indicate that average P_2O_5 contents range from less than 0.1% to 0.3%. This compares to the Clarke number of 0.1050% (Clarke and Washington, 1924). The concentration of P_2O_5 in coal ashes is often higher than 0.3%. This is probably because some, maybe most, of the phosphorus reporting as P_2O_5 in the ash is actually derived from the coal part of the sample. It certainly appears that the phosphorus in a coal seam can not all be attributed to the ash in the coal if the ash has an average shale content of phosphorus (0.065% or 650 ppm P). This would account for 130 ppm in a coal seam with 20% ash which is low compared to the data in Table 1.

TONSTEIN SOURCE

Tonsteins have been studied as potential stratigraphic markers in coal seams. It is generally believed that most of them are of volcanic origin and that they therefore represent ideal time lines preserved in the coal seams. They could also be ash layers derived from forest fires (B.N. Church, personal communication, 1995). In this case they still provide time lines in the coal seam, but will probably be less extensive than a volcanic ash. In rocks adjacent to the coal seams, the more turbulent and rapid conditions of deposition result in mixing of the ash with other sediments and discrete tonstein bands do not survive. Some tonsteins contain phosphatic minerals and could be a source of phosphorus in coal seams.

A number of authors report oxide analyses on tonsteins from around the world (Table 5).

Generally the P_2O_5% concentrations are low except for one tonstein in southeast British Columbia (Grieve, 1983) and four from the Hat Creek deposit in central British Columbia (Hill, 1988) which will be discussed later. Phosphorus in the tonsteins averages 0.09% or 900 ppm, ignoring the Hat Creek data. Based on this average concentration, it is unlikely that tonstein bands that are a minor constituent of coal seams can have much effect on

TABLE 4
AVERAGE PHOSPHORUS CONTENTS OF SHALES

Location	count	av P_2O_5	range
Carboniferous coalfield, Wales	63	0.16	0.07-1.24
As above <0.5µ size	63	0.28	0.07-1.26
Shale	78	0.17	
Shale	277	0.16	
Paleozoic, Europe	36	0.117	
Paleozoic, Japan	14	0.047	
Mesozoic, Japan	10	0.105	
AVERAGE P_2O_5 % total count 541		0.148	
AVERAGE P %			0.0646 or 646 ppm
Data from table 15-K-1 in Wedepohl (1978)			

TABLE 5
PHOSPHORUS CONCENTRATIONS IN TONSTEINS

Location	Count	Av P_2O_5	Range	Reference
NE BC	43	0.19	0.02 - 0.96	Kilby (1984)
China	17	0.0164	003 - 0.104	Burger *et al.* (1990)
SE BC	7	0.0457	0.02 - 0.1	Ryan and Grieve, this study
SE BC	1	4.5		Grieve (1983)
Spain	1	0.091		Bieg and Burger (1992)
South Africa	1	1.97		Spears *et al.* (1988)
Hat Creek	4	11.53	.49 - 15.58	Hill (1988)
WEIGHTED AVERAGE 0.083 % P_2O_5				
AVERAGE P% 0.365 or 3620 ppm				
Average minus Hat Creek data is 0.22% P				

TABLE 6

PHOSPHORUS LEVELS IN VEGETATION

	Loblolly Pine	Pine	Spruce	Beech	White Oak	Red Oak	Hickory	P ppm in coal
Phosphorous in ppm								
STEM		130			130	130	130	230
ROOT								
wood	77			170				220
bark	330			220				490
TRUNK								
wood	47		49	110				125
bark	300		350	650				775
BRANCHES		220			280	320	380	535
wood	50			220				240
bark	620		140	700				870
TWIGS					390	490	580	870
wood	240			700				840
bark	620							1110
needles	11000		1300					2140
leaves		1080		1300	132	1080	1400	2760
buds				2300				4110
AVERAGE VEGETATION				2000				3570

Phosphorus data for vegetation is converted to concentrations in coal assuming
1 No loss of phosphorus.
2 Average carbon in vegetation is 48%.
3 Average carbon in coal is 85%.

the phosphorus content of the whole seam. Spears *et al.* (1988) analyzed a Permian tonstein from West Waterberg, South Africa which has a concentration of 1.97% P_2O_5. They suggested that the phosphorus may have originated outside the volcanic ash, in the adjacent organic matter. The anion PO_4^- is precipitated in the ash with cations such as Ca^{++}, Sr^{++} and Ba^{++} because of lack of competition from other anions such as SO_4^- which, if present, would have used up the available supply of cations. The same suggestion is made by Spears and Kanaris-Sotiriou (1979) to explain why the phosphorus content of ten out of thirty-one European tonsteins averaged 4.36% P_2O_5. Triplehorn (1990) states that aluminum phosphate minerals of the crandallite group (crandallite, gorceixite and goyazite) have been recognized replacing kaolinite in tonsteins. Hill (1988) discusses the possible mobilization of phosphorus into the tonsteins and suggests obliquely that it might come from guano deposits. Based on the high concentrations of barium and strontium in the Hat Creek tonsteins, he identified crandallite and goyazite, often in association with either siderite or ankerite. The suggestion that phosphorus in tonsteins comes from the coal is important because it implies the existence of a mechanism for extracting it from the vegetation before it is turned into coal.

Kilby (1984) studied tonstiens from Lower Cretaceous coals in northeast British Columbia and reports 58 analyses which average 0.19% P_2O_5 (0.083% P). Apatite was reported in about 20 samples and gorceixite in seven of the samples (Kilby, 1983). The P_2O_5 /CaO ratio indicates that there is excess CaO in the rocks over that required to make apatite. Analyses of 20 tonsteins and ash bands collected during this study average 0.09% P_2O_5 (0.039% P). The P_2O_5 /CaO ratio indicates that, in most cases, there is sufficient CaO to account for all the phosphorus as apatite. This does not mean that the mineral is present, in fact x-ray diffraction work did not identify any phosphorus minerals. Of the twenty samples, five are specifically identified as tonsteins and they average 0.058% phosphorus, a value not noticeably higher than that expected for average shales.

It appears that tonsteins and ash bands in the Cretaceous coals in British Columbia generally have low concentrations of phosphorus, often lower than the surrounding coal. Exceptions are found in the southeast where Grieve (1983) reports an analysis on a single tonstein with 4.5% P_2O_5, BaO >0.5% and SrO >0.5%, indicating the presence of gorceixite. At Hat Creek, Hill (1988) reports four tonstein samples which average 11.53 % P_2O_5 and contain crandallite; despite this, Hat Creek lignite is generally not enriched in phosphorus.

VEGETATION SOURCE

Phosphorus occurs in vegetation in low concentrations and is an essential nutrient. Salisbury and Ross (1969) state that higher plants require about 0.2%. Data from this and other sources are compiled in Table 6. The carbon content of the vegetation must also be known before phosphorus contents in vegetation can be compared to contents in coal. Based on data from Ledig and Botkin (1974), the carbon content of dry conifers is about 49.6% and for hardwoods varies from 50% to 53% on a dry basis (Shah *et al.*, 1992). This implies a phosphorus to carbon ratio of about 0.004. Medium-volatile bituminous coals have over 85% carbon on a dry ash-free basis so, if all the phosphorus stays in the coal and the same P/C ratio is maintained, 0.2% phosphorus in vegetation will be equivalent to about 0.36% phosphorus in a coal free of extraneous ash.

Grasses probably have a higher P/C ratio than trees (Marschner, 1986) and this implies possible phosphorus contents in coal averaging over 0.5% (5000 ppm). Contents in dry samples of wheat range from 0.3% to 0.5%, and Wedepohl (1978) provides a table (Table 15-L-7) which lists concentrations for a number of small plants that range from 0.1% to 0.645% on a dry basis.

The phosphorus concentrations in vegetation and the predicted concentrations in coal based upon these levels, assuming no loss of phosphorus, are higher than average concentrations seen in British Columbia coals which are generally less than 0.1% (Grieve, 1992). It appears that there may be a process at work that removes phosphorus during coalification.

Generally there is more phosphorus in deciduous trees than pines and it is not uniformly distributed within a single species. In trees it is concentrated in bark and leaves of a number of different species (Table 6, Kramer

and Kozlowski, 1979). This is because the element is an essential plant nutrient and is usually found in those parts of the plant that grow most rapidly. It is also probable that plants growing in difficult climates require more to survive. Plants extract the phosphorus from the soils as orthophosphate derived from minerals such as apatite which is soluble in acid soils.

In a swamp environment, the phosphorus could be recycled upwards from the dead vegetation into the overlying growing vegetation, effectively migrating upwards through the swamp. This may influence its distribution within the coal seam. The concentration of phosphorus in different parts of plants will also influence its distribution in macerals in the coal and any process that separates the macerals may also separate the phosphorus.

OTHER SOURCES

Other sources of phosphorus include guano or animal remains and extraneous grains of phosphatic minerals which may be of volcanic origin or originate from basement rocks. Isolated grains of phosphatic minerals, such as monazite, or animal-derived material, will cause an erratic distribution of phosphorus *versus* ash in the coal seam. This type of phosphorus is probably responsible for the occasional very high values for some samples, irrespective of their ash content. Bones and guano generally have more than 10% P_2O_5. Inorganic phosphorus may be introduced as single isolated grains of minerals such as apatite (17% P) or monazite (12.4% P). In this case, phosphorus may correlate with the presence of fluorine, calcium or thorium. The presence of monazite probably indicates an inorganic origin for the phosphorus. Monazite derived from basement rocks often survives as a detrital mineral in sands, eventually being deposited in the coal swamp. Finkleman (1980) states that monazite is generally inorganic, but that if it is authogenic it is characterized by low thorium contents. Apatite, on the other hand, is more often authogenic and the phosphorus may have originated in the vegetation.

If phosphorus is concentrated in apatite, then a single grain of apatite embedded in the coal may noticeably increase the phosphorus content of the sample while having very little effect on the overall ash content. For example, if 0.1% apatite dispersed as discrete grains is added to coal which has a phosphorus content of 0.05% then this will contribute an additional 0.017% phosphorus to the 0.05% already present, increasing the concentration by 36%.

MOBILIZATION AND REDEPOSITION OF PHOSPHORUS

The amount of phosphorus in coal probably depends, in large part, on the amount in the original vegetation, and on how much of this was mobilized and removed from the coal swamp during early diagenesis. The phosphorus removed from the organic material in the swamp may well be deposited in footwall or hangingwall material, or in ash bands (tonsteins) within the coal. High levels in these materials, or in coal adjacent to them, may be evidence of removal of phosphorus from the rest of the seam rather than contamination of the seam with phosphorus from the surrounding rocks, which generally have low concentrations.

Two basic ways of removing phosphorus from vegetation in a swamp environment are discussed. One invokes mobilizing it by inorganic means at depth in the swamp and the other by using bacteria or fungi at or near the surface.

The removal of phosphorus at depth by inorganic processes probably takes place when the leaf, bark and twig material that contains most of the phosphorus is reduced to a gel in anaerobic and possibly acid conditions. The gel later becomes the maceral vitrinite. Under these conditions, Swain (1970) suggests that the phosphorus breaks down to orthophosphate (HPO_4^-) and is removed from the rotting vegetation. Organic and inorganic phosphorus can also be dissolved by humic acids generated by the decay of vegetation in anaerobic and acid conditions. Solubility increases in acidified water, especially if concentrations of ferric iron are low, because it tends to form insoluble compounds with phosphorus (Patrick and Khalid, 1974). It appears that phosphorus can be dissolved from organic or inorganic sources in acid or non-acid environments, but it is probably more mobile in acid environments low in ferric iron and calcium-rich clays which can fix phosphorus.

Phosphorus in vegetation can be removed (mineralized) by the action of fungus and bacteria which both generally prefer higher pH conditions that exist near the surface of the swamp. The oxidizing action of bacteria and fungi are responsible, in part, for forming the inert macerals in the coal.

Phosphorus can be fixed organically or inorganically in peat or lignite. Powell (1987) suggests that ionic potential (cation charge/ionic radius) can be used to separate elements into organic and inorganic affinities. He states that P^{3+} is organically bound whereas P^{5+} is more likely to be bound in a phosphate mineral. Thus the trend from acid swamp conditions to less acid, early coal seam environments will be accompanied by a tendency for organic phosphorus to form phosphate minerals.

Inert macerals, in which the vegetation is reduced to a carbon skeleton, are formed by bacterial or fungal attack, or by forest fires. The macerals obviously form in aerobic conditions at the expense of material that would otherwise form vitrinite. The resultant carbonized material retains the original cell structure and probably most of the phosphorus, because it is not volatilized during burning. The maceral will therefore, initially, always have a better mesoporosity (phyteral porosity) than the vitrinite maceral. Phyteral porosity often forms long cylinder-like cavities which are the remains of the cell structures (cell lumen, Gamson *et al.*, 1993). Porosity is maintained in the inert macerals while the vitrinite material is going through a jellification process and has limited porosity. The inert macerals will therefore offer a

ready site for the redeposition of phosphorus, as a mineral, at a time when it is most mobile in the pre-coal material. Phosphorus in Australian coals is common as a cell infilling (Cook, 1962; Kemezys and Taylor, 1964) and may therefore concentrate in the inert macerals. Mobilized phosphorus may well crystallize as crandallite group minerals, such as goyazite, based on the good correlation with strontium in coals studied by Gluskoter *et al.* (1977), Harris *et al.* (1981) and Hill (1990) (Table 3).

It is possible that some mobilized phosphorus does not find a home in the inert maceral porosity and it is not clear where it goes. One possibility is that it is recycled upwards, through the decaying vegetation, and continuously reused by the living plants. It may therefore be enriched in hangingwall coal or rock. This has not been seen in this study but is apparent in some of the seam profiles of Gluskoter *et al.* (1977). Spears *et al.* (1988) have suggested a process by which phosphorus can precipitate as a phosphate in adjacent tonstein or ash bands.

The amount of phosphorus in a seam will depend, in part, on the composition of the original vegetation and on how effectively it is mobilized out of the vegetation (proto-vitrinite) and deposited in inert macerals or removed from the swamp. In the absence of a process that forms inert macerals, coals derived from a high proportion of bark, leaves and small plants will be characterized by high contents of formless vitrinite and high contents of organically bound phosphorus that will be very difficult to wash out. Local variations of phosphorus concentrations within the seam may correlate with the inert maceral content in the coal. High contents may be found in fusinite which has the best developed phyteral porosity. Other inert macerals probably lost some of their organic phosphorus by bacterial or fungal activity, but have had secondary phosphorus deposited in the phyteral porosity and may now contain more than the adjacent vitrinite macerals.

It is unlikely that phosphorus is introduced into the coal seam after diagenesis. As the rank increases from lignite to low-volatile bituminous there is a decrease in mass of at least 20% because of the loss of volatile matter. This results in an equivalent increase in concentration of phosphorus from low to high rank coals. In most low rank coals, organic derived phosphorus may show an organic affinity and specifically be concentrated in the inertinite macerals as finely dispersed phosphatic minerals. Over time, as conditions become less reducing, phosphorus may be mobilized and, unable to find porosity in the coal, move out into ash bands, roof or floor rock. There is some indication that phosphorus as carbonate-apitite can deposit on cleats in the latter stages of their formation (Spears and Caswell, 1986). In this study there is a tendency for phosphorus to be associated with siderite which Spears and Caswell consider to be an early diagenetic mineral. The phosphorus associated with oolitic or banded siderite may be mobilized during early biogenic coalification, indicating a diagenetic mobility of phosphorus in association with iron. In acidic conditions, high concentrations of Fe^{++} help to keep the phosphorus

in solution. If these solutions move into higher pH environments then siderite and phosphate minerals may precipitate.

THEORETICAL PHOSPHORUS VERSUS ASH DISTRIBUTIONS

A phosphorus (y axis) *versus* ash (x axis) plot can be used to illustrate various associations of phosphorus in coal, such as the four locations illustrated in Figure 3. If the phosphorus is uniformly distributed in the ash or coal part of the sample, then a plot of the data will scatter along a line with positive slope if it is in the ash and a negative slope if it is in the coal.

The amount of compaction experienced by coal depends on the amount of ash in it. This means that, if phosphorus is introduced into the coal swamp as random extraneous grains, as distinct from ash, then the concentration will increase in the low-ash coal because of increased compaction. Coal compacts at least five times more than adjacent rock and therefore the concentration will be increased by a similar factor in low-ash coal compared to ash bands. In this case phosphorus *versus* ash plots will imply that the phosphorus originates in the coal, which it did not.

Cleats are preferentially developed in low-ash coal and in bright vitrinite-rich lithotypes. Consequently if phosphorus is concentrated on cleats (Spears and Caswell, 1986) then concentrations will increase markedly as ash contents decrease and as the amount of vitrinite in the sample increases.

With the introduction of the possibility of inhomogeneous distribution of phosphorus in porosity in the organic part of the sample, more complicated plots are possible, especially as there is often a correlation between the ash content and the reactives/inerts maceral ratio in the coal, which tends to increase as the ash content decreases. This is illustrated in Figure 4, using data from a number of sources (Gates Formation, northeast British Columbia, Lamberson and Bustin, 1993; Greenhills mine, Holuszko, 1993 and Lower Mist Mountain Formation, Dawson *et al.*, 1994). All the plots show a tendency for the reactives/inerts ratio to increase as the ash decreases below about 10%. If phosphorus is concentrated in the inert macerals, and the reactives/inert

TABLE 7
PHOSPHORUS CONTENTS IN COAL LITHOTYPES

Coal type	count	P ppm	Location
Durite	5	140	Ruhr Area, West Germany
Vitrite	?	200	Upper Silesia, Poland
Vitrite	6	110	Ruhr Area, West Germany
Chanel Coal	3	600	as above
Boghead coal	1	600	as above
Fusite	3	1 100	as above
Fusite	3	99 000*	Upper Silesia, Poland
Fusite	20	5 700	Central England

* concentration in ash, concentration in coal probably 5 to 10 times lower.

Data from Table 15-L-10 in Wedepohl (1978).
References are listed in the same publication.

DULL AND BRIGHT LITHOTYPES HAND PICKED FROM SEAMS G AND J

| Sample	Yield	H₂O	VM%	Ash%	FC%	P%	TS	PS	SS	OS
G dull raw	100	0.60	22.8	16.48	60.12	0.92	0.30	0.03	0.01	0.26
G dull wash	92.29	0.62	22.9	15.10	61.34	0.24				
G dull sink	7.71			33.00		9.06				
G bright raw	100	0.84	24.5	5.26	69.42	0.06	0.36	0.01	0.01	0.35
G bright wash	99.2	0.6	22.8	5.22	71.35	0.07				
G bright sink	0.8			10.2		0				
J dull raw	100	0.68	24.9	23.25	51.53	0.15	0.50	0.02	0.01	0.48
J dull wash	79.16	0.60	26.3	20.25	52.89	0.16				
J dull sink	20.84			34.65		0.11				
J bright raw	100	0.69	28.4	9.28	61.66	0.16	0.52	0.01	0.01	0.51
J bright wash	91.88	1.81	29.8	5.8	62.57	0.13				
J bright sink	8.12			48.7		0.5				
sink data calculated		TS = total sulphur		PS = pyritic sulphur		SS = sulphate sulphur		OS = organic sulphur			
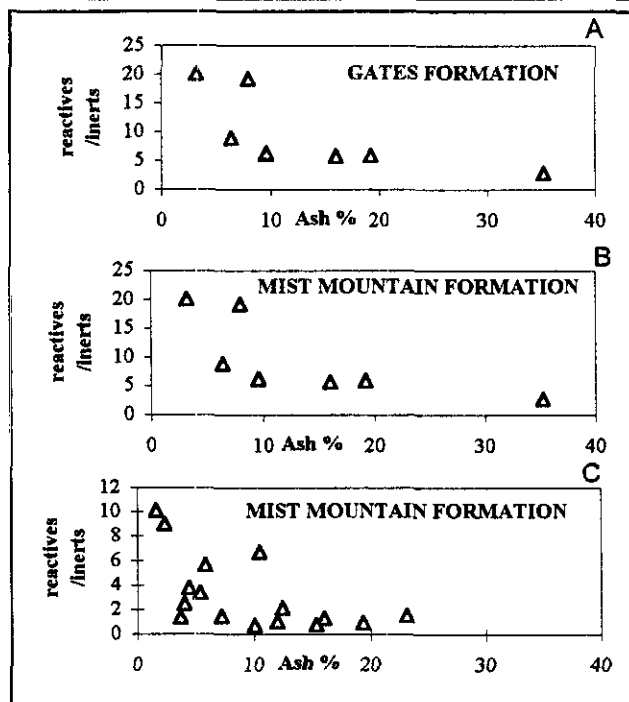
Figure 4. Plots of reactives/inerts ratio *versus* ash content for some British Columbian coals. Data from Lamberson and Bustin (1993)(A), Holuszko (1993)(B) and Dawson *et al.* (1994)(C).

ratio increases as ash content decreases, then the phosphorus concentration reaches a maximum at intermediate ash contents. This is an important distinction from the other plot patterns.

EVIDENCE FOR A LITHOTYPE AND MACERAL CONTROL ON PHOSPHORUS DISTRIBUTION

There is some evidence in the literature for a lithotype control on the distribution of phosphorus in coal, but it is by no means unambiguous. A number of references are mentioned by Wedpohl (1978), many of which were previously cited by Gmelin (1965). The data (Table 7) indicate that the phosphorus is concentrated in fusite by a factor of five to ten times compared to vitrite. Berger (1958) studied some Russian coals and noted that the concentration of phosphorus in bright coals was eight to ten times less than in dull coals, which are usually ash or inert-maceral rich.

Harris *et al.* (1981) studied the distribution of elements in channel samples through two high-volatile coal seams of Middle Pennsylvanian age in eastern Tennessee. Their paper provides lithotype and petrographic data on an incremental basis though the two seams. There is a tendency for high phosphorus concentrations to correlate with high contents of dull lithotypes and inert macerals, and low contents to correlate with high ash contents. There is a strong correlation of phosphorus with strontium which has been seen in a number of datasets and is interpreted to indicate that much of the phosphorus is occurring as goyazite, which is probably an early diagenic mineral.

During the channel sampling at one of the mines, samples of dull and bright lithotypes were collected from seams G and J (Table 8). In seam G the phosphorus content is high and strongly concentrated in the dull lithotype (0.92% P) which contains three times as much ash as the bright lithotype. A 1.5 specific gravity float of the dull lithotype reduced the phosphorus to 0.24% but had little effect on the ash. The calculated composition of the sink material is 9.06% phosphorus and 33 % ash. At this phosphorus concentration, the sink material must contain a high percentage of phosphatic minerals. The dull lithotype from seam J contains much less phosphorus (0.15% P) and about the same amount as the bright lithotype from the seam. Neither the ash nor phosphorus were removed by washing at 1.5 SG. More data are required, but it appears that high phosphorus concentrations are associated with the dull lithotypes and not with the ash in the dull lithotypes.

Run-of-mine and product coal samples from G seam were collected during this study. Samples were screened to various sizes and analysed for phosphorus. In addition, the size fractions of the ROM coal were washed at 1.5 SG and also analysed (Table 9, Figure 5). The ROM coal has ash and phosphorus concentrations of 22% and 0.17%, which are reduced to 8.8% and 0.16% by washing in the plant. Obviously the plant is effective at removing ash, but not phosphorus, which does not follow the ash. This could be surprising because there is a strong correlation between phosphorus *versus* ash for the raw size fractions (Figure 5A). This must be an artifact of the data because,
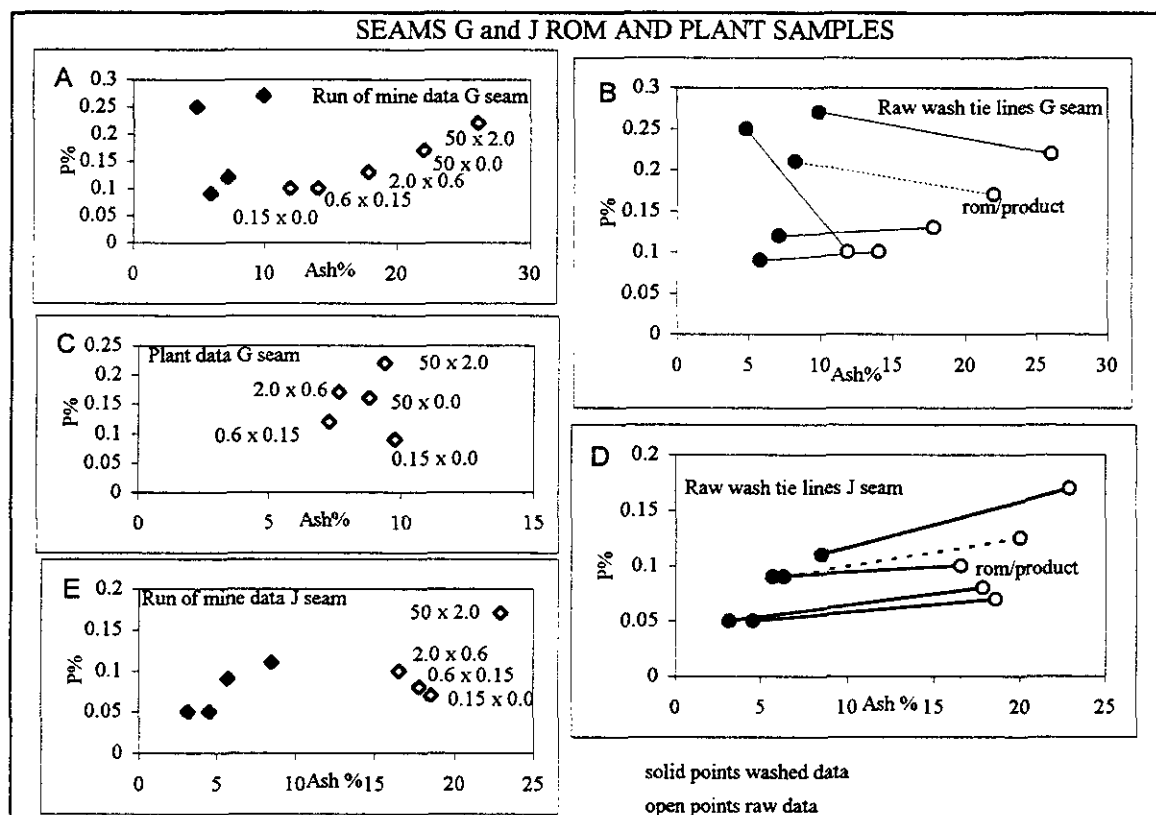
Figure 5. Plots of phosphorus *versus* ash for G and J seam washability data.

TABLE 9
SEAMS G AND J WASHABILITY DATA
All data air-dried basis

Sample	Weight	float	Yield	H₂O%	VM%	Ash%	FC%	P%
			Run of mine G seam					
raw coal	100		100	0.83	20.08	22.01	57.1	0.17
50 x 2.0mm	59.55		100	0.78		18.03		0.22
50 x 2.0mm		1.5 S	65.42	0.75		9.94		0.27
2.0 x 0.6mm	17.15		100	0.87		17.87		0.13
2.0 x 0.6mm		1.5 S	79.75	1.19		7.22		0.12
0.6 x 0.15m	13.27		100	1		14.08		0.1
0.6 x 0.15mm		1.5 S	83.57	2.12		5.92		0.09
0.15 x 0mm	10.03		100	1		11.96		0.1
0.15 x 0mm		1.5 S	66.33	3		4.89		0.25

Sample	Weight	float	Yield	H₂O%	VM%	Ash%	FC%	P%
			Plant Product G seam					
wash coal	100		100	0.99	21.16	8.83	69	0.16
50 x 2.0mm	37.06		100	0.98		9.39		0.22
2.0 x 0.6mm	19.29		100	1		7.7		0.17
0.6 x 0.15m	20.81		100	1.07		7.31		0.12
0.15 x 0mm	22.84		100	1.15		9.79		0.09

Sample	Weight	float	Yield	H₂O%	VM%	Ash%	FC%	P%
			Run of mine J seam					
raw coal	100		100	0.92	27.17	20.43	51.5	0.08
50 x 2.0mm	46.15		100	0.9		22.93		0.17
50 x 2.0mm		1.5 S	71.85	0.6		8.53		0.11
2.0 x 0.6mm	22.33		100	0.88		16.55		0.1
2.0 x 0.6mm		1.5 S	81.34	0.74		5.73		0.09
0.6 x 0.15m	18.61		100	0.92		17.83		0.08
0.6 x 0.15mm		1.5 S	76.22	0.87		3.21		0.05
0.15 x 0mm	12.9		100	1.05		18.57		0.07
0.15 x 0mm		1.5 S	62.97	0.77		4.59		0.05

when the product coal is plotted in Figure 5C, there is a wide variation of phosphorus contents but little change in ash content.

The underlying control on phosphorus content is not the ash but the inert maceral content of the coal which increases in the coarse size fractions in both the ROM and washed coal. The vitrinite maceral is more brittle and always fractures into smaller fragments and concentrates in the finer sizes when a sample is crushed and screened. Both the ash and the phosphorus tend to locate in the phyteral porosity in the inert macerals, but it is more difficult to dislodge phosphorus than ash. Consequently the ROM data appear to indicate an ash affinity for the phosphorus when, in fact, both the ash and phosphorus have an affinity for the porosity in the inert macerals which concentrate in the coarser sized coal once it is crushed and screened.

The maceral compositions of the G seam samples described in Table 9 were determined (Table 10). The results are preliminary, are based on 500 point counts per sample and are expressed on a mineral-matter-free basis. Inert macerals are concentrated in the coarser size fractions and the inert maceral content correlates with phosphorus in the samples. Mineral infilling in the cells preserved in the fusinite and semifusinite is clearly visible and based on the correlation in Figure 6 must consist largely of a phosphorus mineral.

The petrography for samples from southeast British Columbia was determined in Dawson *et al.* (1994). These samples were analysed for phosphorus during this study, to make use of the existing petrographic information. The samples (Table 11, Figure 7) are from seams A lower, A upper, P and Y. Individual samples were separated into a number of SG splits; raw(r), 1.4 SG float(f), 1.4-1.6 SG middlings(m) and 1.6 SG sink(s).

TABLE 10
PETROGRAPHY FOR G SEAM, WASHABILITY DATA

sample	mineral matter free maceral percentages					
	Vitrinite A	B	Semi Fusinite	fusinite	Total reactives	Total inerts
run-of-mine G seam						
50 x 0.0mm R	52.4	20.9	21.8	4.5	73.3	26.3
50 x 2.0mm R	47.1	23.3	19.4	10	70.4	29.4
50 x 2.0 F	31.1	31.9	24.8	12.1	63	36.9
2.0 x 0.6m R	52	21	21.2	5.6	73	26.8
2.0 x 0.6m F	46.1	28.8	18.7	6.3	74.9	25
0.6 x 0.15m R	55.3	24.6	15.5	3.3	79.9	18.8
0.6 x 0.15m F	46.7	34.7	14	3.3	81.4	17.3
plant product G seam						
50 x 2.0mm W	25	51.3	17.4	6.4	76.3	23.8
2.0 x 0.6m W	44.3	25.8	25.8	3.1	70.1	28.9
0.6 x 0.15m W	46.9	41.5	6.3	5.3	88.4	11.6

R = raw sample F= 1.5 SG float sample
W= plant washed sample
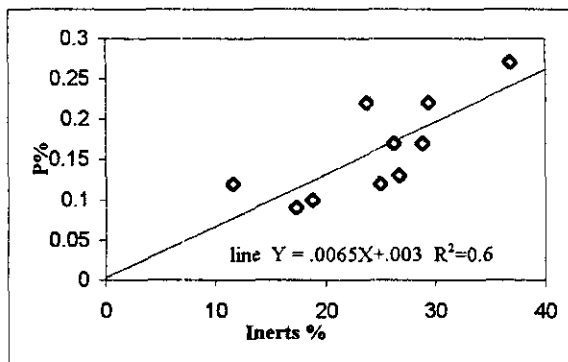
Figure 6. Plot of phosphorus *versus* inerts for G seam, washability samples.

The middling splits are enriched in the inert macerals relative to other splits from the same seam and consequently there is a range of maceral composition for the splits from each seam. Attempts were made, using the four splits from each seam, to predict the phosphorus content of each split by assigning phosphorus concentrations to the ash, reactive and inert components of each split. In sample A lower, the phosphorus is uniformly distributed, whereas in seams P and Y it is concentrated in the inerts. A plot of predicted *versus* measured phosphorus (Figure 7) indicates that apart from one split, a good match is achieved. Split Y(sink) obviously contains phosphorus liberated from the other Y seam splits. The data appear to indicate that phosphorus is preferentially concentrated in the inert macerals in each seam, although in some cases it is coarse enough to be liberated and its original association is not known. It is interesting to note that if all the data are examined on a phosphorus *versus* inert maceral plot, there is no apparent relationship because of the wide range of concentrations in the inert macerals from the different seams.

The data of Gluskoter *et al.* (1977) can be interpreted to indicate a maceral control on the phosphorus concentrations in the samples they considered to have organic affinity. They studied the organic *versus* inorganic affinity of phosphorus in eight
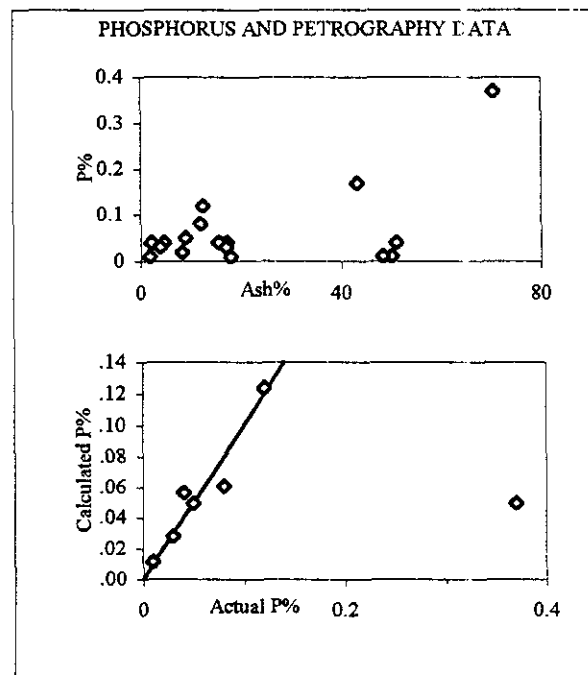

Figure 7. Phosphorus and ash data for different specific gravity splits of samples. Data from Dawson *et al.* (1994).

samples, by measuring the concentration in different density splits. Obviously the ash increases as the density increases and, if the concentration of phosphorus also increases with specific gravity then this indicates an ash affinity and the reverse indicates an organic affinity. Of the eight samples analyzed, Gluskoter assigned five samples organic affinity, one intermediate and two inorganic affinity. It is interesting to plot the phosphorus contents *versus* specific gravity for each sample (Figure 8). Two plots show a trend of continuously increasing phosphorus concentration as the specific gravity increases. Some of the other plots actually show a maximum phosphorus concentration at intermediate values. This indicates an organic affinity, but it is surprising that the maximum phosphorus concentration does not occur in the lowest density sample with the lowest ash.
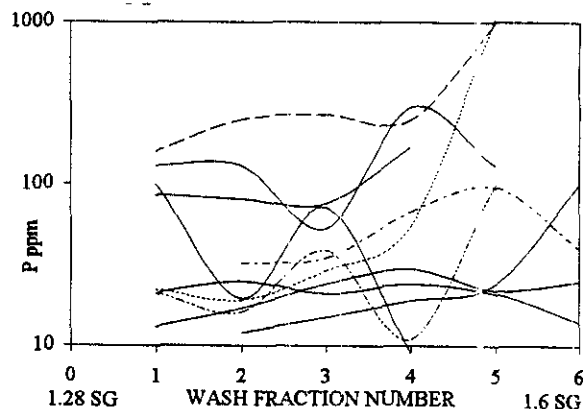

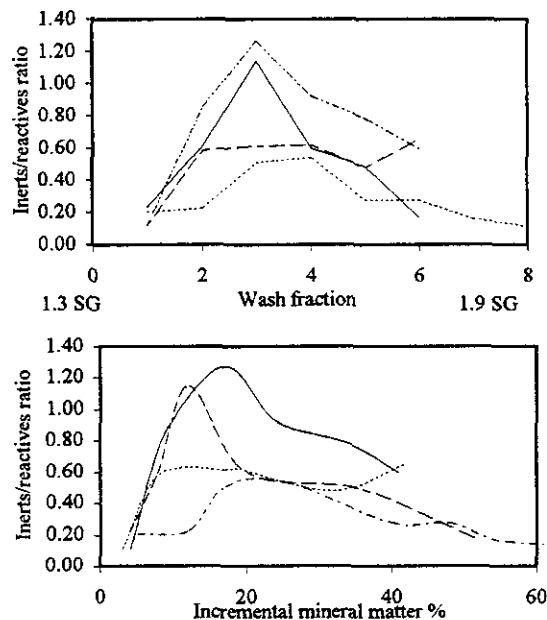Figure 8. Phosphorus *versus* specific gravity plots for data from Gluskoter *et al.* (1977).

Figure 9. Plot of inerts/vitrinite ratio *versus* specific gravity and incremental ash. Data from Bustin (1982).

Sample	yield	ash	P%	TR	TI	ratio I/R	SR	SI	P%[f]
best fit P concentrations			ash= .040			reacts= .040		inerts= .040	
A-1/r	100.0	17.12	.040	57	43	0.75	47.24	35.64	.040
A-1/f	41.6	4.61	.040	79	21	0.27	75.36	20.03	.040
A-1/m	41.8	15.38	.040	44	56	1.27	37.23	47.39	.040
A-1/s	16.6	50.92	.040	48	52	1.08	23.56	25.52	.040
A-2/r	100.0	16.98	.030	47	53	1.13	39.02	44.00	.042
A-2/f	28.9	8.19	.020	NA	NA				
A-2/m	60.5	17.88	.010	NA	NA				
A-2/s	10.6	43.24	.170	calc	NA				
best fit P concentrations			ash= .006			react= 0		inerts= 0.09	
P/r	100.0	3.90	.030	71	29	0.41	68.23	27.87	.028
P/f	76.2	1.80	.010	91	9	0.10	89.36	8.84	.012
P/m	21.8	8.87	.050	42	58	1.38	38.27	52.86	.050
P/s		2.0	48.20	.011	calc				.003
best fit P concentrations			ash= .000			react= 0		inerts= 0.40	
Y/r	100.0	12.02	.080	87	13	0.15	76.54	11.44	.061
Y/f	77.9	2.12	.040	90	10	0.11	88.09	9.79	.057
Y/m	11.6	12.50	.120	68	32	0.47	59.50	28.00	.124
Y/s	10.5	70.46	.370	61	39	0.64	18.02	11.52	.050

calc = data calculated P%[f] calculated P	r = raw data
TR = total reactives mineral-matter-free basis	f = float data
TI = total inerts mineral-matter-free basis	m = middlings data
SR = reactives in sample	s = sink data
SI = inerts in sample	

Washing a coal at different specific gravities produces maceral fractionation in which the inerts/vitrinite ratio reaches a maximum at intermediate values, as illustrated by data in Table 11 and from Bustin (1982; Figure 9). If the phosphorus is concentrated in the inert macerals then this explains the phosphorus-ash relationships obtained by Gluskoter *et al*. It appears that in a group of samples with a range of ash contents, either naturally occurring (Figure 4) or produced by washing the samples (Figure 9), the inert /reactives ratio will be at a maximum at intermediate ash concentrations. In both cases, if phosphorus is concentrated in the inert macerals then a maximum will occur in samples of intermediate ash concentration.

Many phosphorus *versus* ash and phosphorus *versus* specific gravity distributions can be explained by an inhomegeous distribution of phosphorus between the coal macerals. Because of the preference for both phosphorus and ash to locate in the inert macerals, phosphorus sometimes appears to have an ash association, but only in samples containing low and intermediate ash concentrations. Also because, the concentration of phosphorus in inerts in different seams varies widely, a phosphorus *versus* inerts relationship may only be apparent in closely related samples.

ASH-PHOSPHORUS DISTRIBUTIONS IN BRITISH COLUMBIAN COALS

There are a number of datasets for coals from British Columbia that can be used to illustrate data patterns in phosphorus *versus* ash plots (Figure 10). Data for Tertiary lignites from Hat Creek (Hill, 1990) form a scatter with maximum phosphorus at about 25% ash and less in samples with more or less ash. Data for high-volatile coals comes from the Cretaceous Telkwa and

Quinsam properties (Matheson *et al.*, 1994) which are of similar age and depositional environment, although Telkwa samples, which contain more inert macerals, have the higher phosphorus concentrations. Data for medium-volatile coals are from the present study and Grieve (1992). Most of the data plot in triangular distributions with maximum phosphorus occurring at intermediate ash concentrations. The Klappan property provides data for high-rank coals (Coal Assessment Reports 110, 111 and 748). These data indicate a weak tendency for phosphorus content to increase as ash content increases. In most of the plots, there is no indication of phosphorus concentrating in the pure coal or ash components of the samples.

The predominance of the triangular scatter pattern is probably caused by a combination of two factors. The phosphorus tends to concentrate in the inert macerals and the reactives/inerts ratio tends to decrease with increasing ash. The combined effect of these two variables is to produce maximum phosphorus concentrations at intermediate ash concentrations as hypothesized by the model developed above.

IN-SEAM PHOSPHORUS VARIATION

As part of this study, incremental seam samples were collected from five sites at one mine and three sites at another. The distribution of phosphorus within a seam may provide clues to its origin, and the information may also be useful if selective mining is considered. Additional data have been collected from a number of sources to provide a database of phosphorus distribution within seams. Samples collected as part of this study were analyzed for raw proximate, sulphur and phosphorus.

AVERAGE QUALITY FROM INCREMENTAL AND GRAB SAMPLE TRENCH DATA
length weighted average data

seam	count	H₂O ad	Ash%	VM%	FC%	TS	PS	SS	OS	P%	Yield	H₂O ad	Ash%	VM%	FC%	P%
A fw	1	0.7	17.56	18.47	63.3					0.07	56.14	0.76	6.28	22.29	70.67	0.04
A hw	1	0.65	10.89	19.52	68.9					0.01	68.53	0.72	5.94	22.26	71.08	0.01
C-1	1	0.58	20.29	21.11	58					0.08	52.51	0.7	6.7	25.52	67.08	0.08
C-2	1	0.59	32.97	16.97	49.5					0.15	38.98	0.68	7.13	21.69	70.5	0.13
D-1	1	0.55	35.2	16.41	47.8					0.17	50.35	0.75	7.44	21.87	69.94	0.2
D-2	1	0.64	32.25	17.22	49.9					0.07	43.75	0.7	7.28	21.55	70.47	0.07
D-3	1	0.65	21.14	19	59.2					0.12	61.62	0.74	5.64	23.49	70.13	0.1
E	10	0.77	14.2	20.95	62.4	0.27	0.013	0.01	0.25	0.15	81.11	0.53	8.81	22.02	66.94	0.103
G-1	12	0.52	17.94	22	59.5	0.5	0.013	0.01	0.49	0.04	75.79	0.41	9.73	22.76	67.1	0.029
G-2	8	0.59	17.78	23.04	58.59					0.20	81.22	0.68	8.76	25.17	65.40	0.18
G¹	1	dry	13.74	23.29	63					0						
I	13	0.94	11	21.06	64.1	0.31	0.01	0.01	0.3	0.08	85.17	0.43	5.34	22.76	68.61	0.086
J-1	3	0.66	31.12	21.92	46.3					0.05	62.92	1.01	7.09	28.21	63.69	0.09
J-2	4	0.55	19.15	22.56	57.75					0.06	76.58	0.52	8.92	24.69	65.88	0.10
L	11	0.9	6.94	24.7	57.4	0.6	0.02	0.01	0.57	0.03	82.85	0.78	4.37	26.14	58.56	0.024
L¹	1	dry	46.17	16.6	37.2					0.081						
O	17	1.16	9.14	31.06	58.6	0.43	0.073	0.02	0.34	0.05	92.85	0.63	5.11	34.22	65.39	0.043

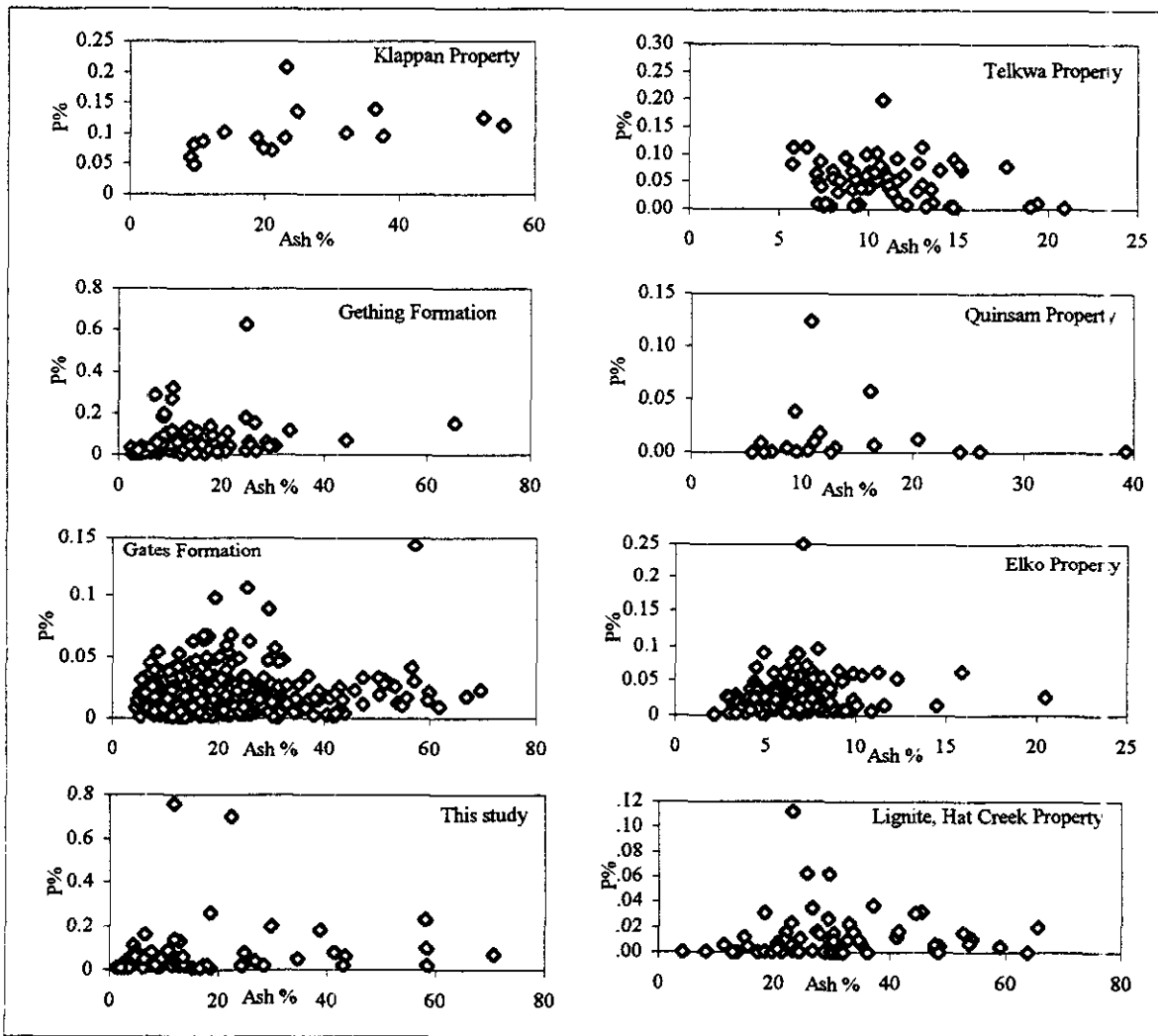G¹ = Data from Bonnell *et al.* (1984)   TS = total; PS = pyitic; SS = sulphate and OS = organic sulphur

Figure 10. Phosphorus *versus* ash distributions for British Columbia coals of different ranks (sources specified in text).
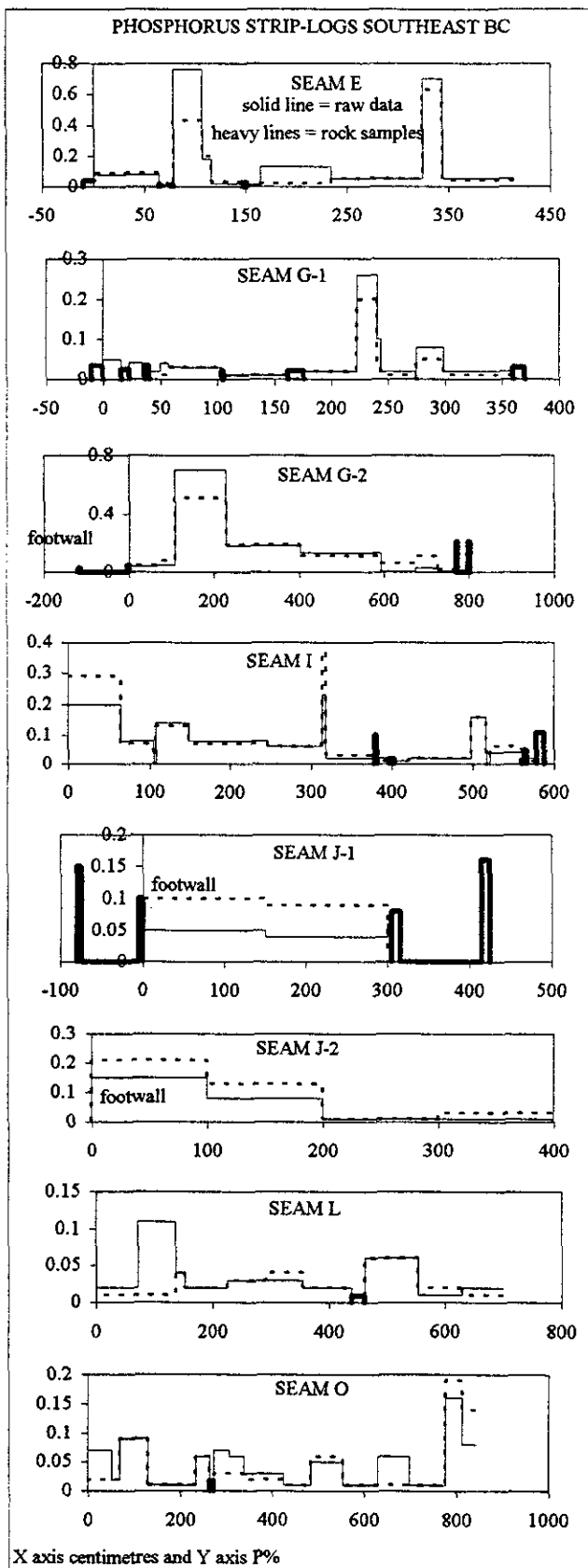
PHOSPHORUS STRIP-LOGS SOUTHEAST BC

Figure 11. Strip-logs of raw and wash phosphorus for data collected during this study.

Samples collected as part of this study were analyzed for raw proximate, sulphur and phosphorus. Samples were then washed at 1.5 SG and analysed for ash and phosphorus. The incremental seam data are summarized in Table 12. Seams sampled include seams E, G, I, J, L and O. Hangingwall rock, footwall rock, ash and tonstein bands were analysed for a full suite of oxides and for mineral identification using x-ray diffraction. The phosphorus and ash data for these seams are displayed as strip-logs in Figure 11, in which the dotted lines represent the wash data and the solid lines the raw data. Rock partings, hangingwall or footwall material are identified by heavy lines. In addition to the data generated during this study, strip-logs for ash and phosphorus are constructed from data from Grieve (1992; Figure 12) in which the samples represent constant increments.

The incremental samples collected as part of this study were delineated based on lithotype, amount of shearing, or obvious ash or tonstein bands. There is a tendency for phosphorus concentrations to increase if:

• The predominant lithotype is dull.
• In the presence of siderite.
• If the coal is sheared.

The lithotype association is in agreement with the data in Table 8 and is best developed in seam G-2 (Figure 11) where the pronounced phosphorus high in the seam corresponds with an outcrop of dull lithotypes. In many of the strip-logs phosphorus has a negative correlation with ash (Figure 12).

There is a tendency seen in some data for phosphorus to increase toward the footwall and hangingwall. There is no evidence in the data collected during this study that the rocks enclosing the seams have a halo of high phosphorus; nor are ash or tonsteins bands within the seams enriched in phosphorus compared to the adjacent coal. In fact, the concentrations in the rocks are similar to those in the whole coal and consequently can only account for about one-fifth of the phosphorus in the coal, assuming 20% ash in the coal. The rest is probably from the vegetation, or possibly from phosphorus-rich fragments, air or water transported into the swamp.

The ash oxide data indicate that there is not enough

TABLE 13
RAW PHOSPHORUS IN THE BASAL SEAM
MIST MOUNTAIN FORMATION

| Location	Seam	Ash	P₂O₅	P in coal
Elkview	Balmer[1]	14.47	1.16	0.073
Elkview	Balmer[1]	15.57	0.74	0.050
Elkview	Balmer[2]	16.8	0.52	0.038
Greenhills	1 seam[1]	26.54	0.04	0.005
Corbin	Mammoth[1]	18.68	0.06	0.005
Corbin	Mammoth[1]	15.82	0	0.000
Byron Creek	Mammoth[3]	21.71	1.16	0.031
Byron Creek	Mammoth[3]	21.32	0.74	0.035
Byron Creek	Mammoth[3]	21.5	0.52	0.013
Line Creek	10 seam[3]	21.1	0.04	0.027
1 = Bonnell et al. (1985) 2 = Goodarzi et al. (1985)				
3 = Grieve (1992)				
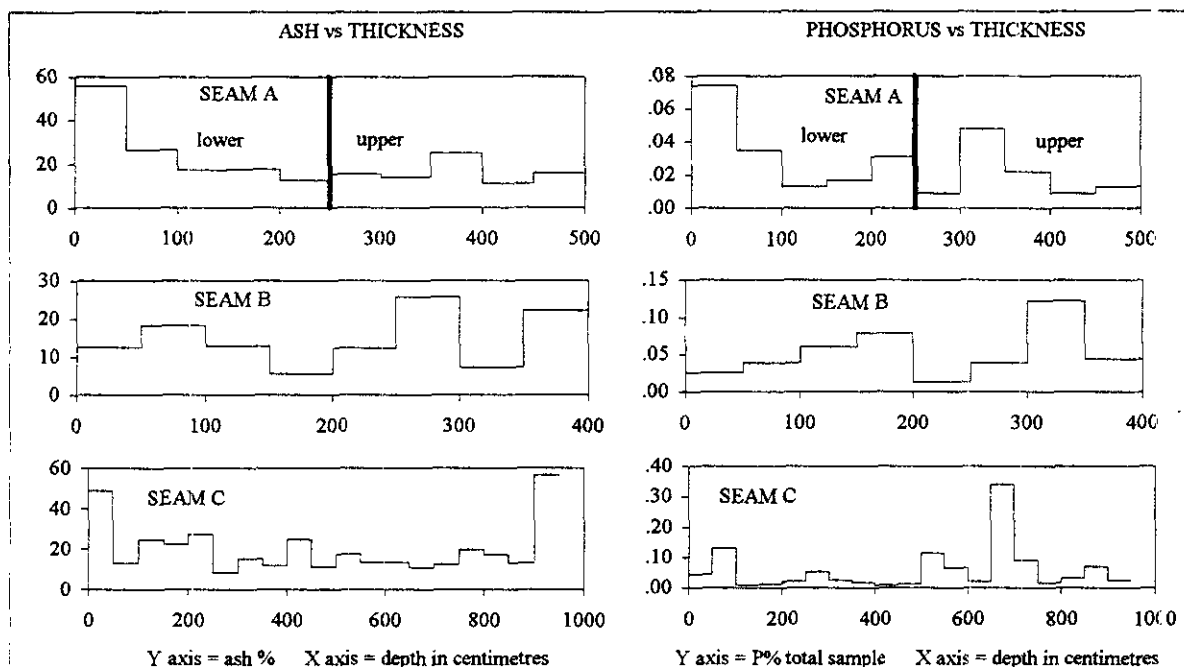
Figure 12. Strip-logs for raw phosphorus and ash. Constructed from data in Grieve (1992).
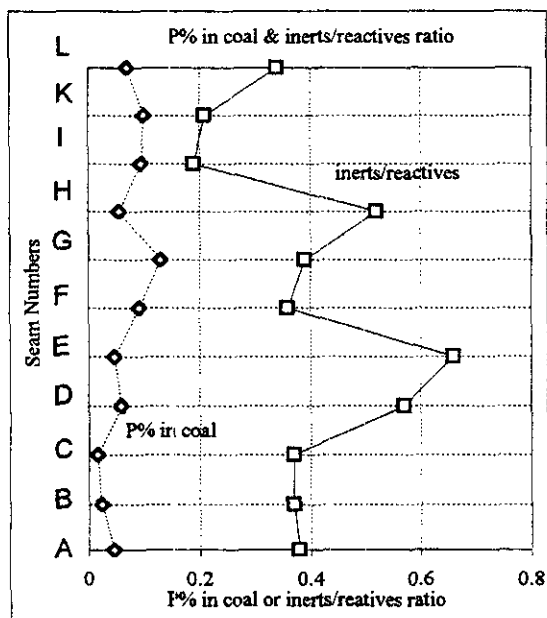

Figure 13. Average P% *versus* inerts/reactives ratio for seams in the lower part of the Mist Mountain Formation.

barium to use all the phosphorus to make gorciexite, but that there is excess CaO over that required to make apatite with all the phosphorus present. Strontium was not analysed for, so it is not known if the phosphorus is present in the mineral goyazite. The x-ray diffraction data did not identify any phosphatic minerals and a majority of the samples contained mainly quartz and kaolinite with anatase (TiO oxide) as a frequent minor mineral.

REGIONAL DISTRIBUTION OF PHOSPHORUS IN MIST MOUNTAIN COALS

Within a single seam, the phosphorus may be concentrated in the inert macerals, but this does not mean that, from seam to seam, there has to be a correlation between concentrations of inert macerals and phosphorus. In fact, the lowest seam in the Mist Mountain section (Mammoth seam) at Coal Mountain (Figure 1) is one of the most inert rich seams in the Mist Mountain Formation, but is not characterized by high phosphorus (Table 13). There is no database of phosphorus and petrographic analyses on a seam by seam basis through the Mist Mountain Formation. It is possible, however, to extract some information from Coal Assessment Reports. Often the phosphorus and petrographic data were obtained from different samples of the same seam, but it is hoped that by averaging the data, simple trends may be apparent. A plot of average phosphorus concentrations *versus* average inert/reactives ratio produces a moderately good negative correlation (Figure 13). Seam numbering is schematic, starts at the base of the Mist Mountain Formation, and does not correspond to nomenclature used at any particular mine. Data were obtained for the lower third of the formation. The high-inert seams are not characterized by high phosphorus.

If the above correlation is real, then it implies that the initial phosphorus loading of a seam is related to vegetation type or conditions outside the coal swamp. The initial development of inert macerals provides porosity and limited permeability for moving the phosphorus, which is strongly concentrated in inert
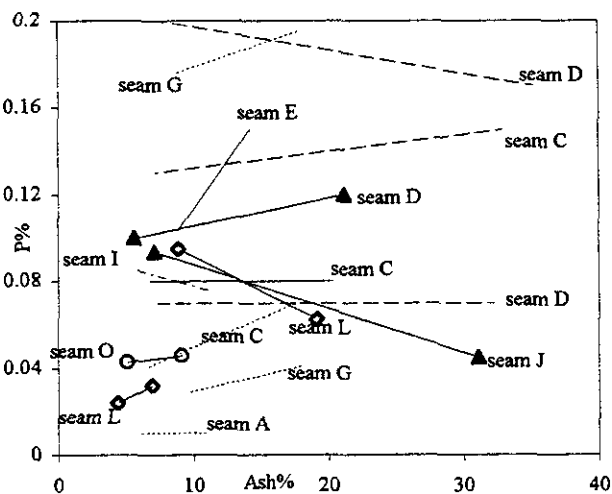
Figure 14 Tie-line plots for average raw and wash phosphorus data from seams studied in this paper.

macerals with respect to reactive macerals, but the overall phosphorus content in the seam remains high. As more inerts are generated, permeability improves and phosphorus moves out of the seam. Consequently, although it is still concentrated in the inerts, the overall concentration in the coal decreases. The petrographic data in Table 11 support this hypothesis. The seam with the highest reactives content also has the most phosphorus and it appears to be strongly concentrated in the inert macerals.

There seems to be a high-phosphorus seam in the lower part of the section in most of the mines in southeast British Columbia. It is approximately the fourth major seam up-section at the mines and the second up-section at the Elko property at the northern end of the Elk Valley coalfield (Grieve, 1992). At present it is not known if the seams represent the same stratigraphic horizon and no reason for the increased phosphorus is postulated. There are some data to suggest that the phosphorus in the lowest seam in the Mist Mountain Formation is consistently low, as illustrated by analyses for coal from Coal Mountain in the south to Greenhills in the north (Table 13).

WASHING CHARACTERISTICS OF PHOSPHORUS AND METHODS OF CONTROL

The washing characteristics of phosphorus are illustrated using a tie-line plot in which raw and wash data, plotted on the same ash *versus* phosphorus plot, are joined by a line (Figure 14). Lines with positive slopes indicate removal of phosphorus during washing and lines with negative slopes indicate that the phosphorus is concentrating in the clean coal.

The incremental data from the eight sampling sites are averaged, based on the length represented by each sample. In addition, grab samples from seams were analysed for raw and wash ash and phosphorus (Table

12). All the data are plotted in Figure 14 with the seam numbers identified. It is apparent that phosphorus behaves inconsistently when washed. Washing concentrates phosphorus in some seams and reduces it slightly in others. The average raw phosphorus contents of the seams range from 0.032% to 0.2% (Table 12) and the wash contents from 0.024% to 0.18%. The ratios of wash to raw phosphorus range from 69% to 167%. In general, washing did not reduce the phosphorus concentration by more than 30%. It is clear that even if phosphorus tends to be associated with ash in the raw samples, it does not follow the ash during washing and is in general more difficult to remove.

Samples for full washability analysis were collected from one of the mine wash plants during a time when a single seam, was being processed. A comparison of the phosphorus in the ROM and product coal (Figures 5 B and D) indicates that the plant was not able to remove much phosphorus. It is also apparent from Figure 5 that phosphorus is concentrated in the coarser size fractions and is very difficult to remove. Even in the finest size, phosphorus is concentrated in the clean coal, indicating that there is little liberation.

The best way of controlling phosphorus in the clean coal may be by blending ROM coal. Another possibility is to wash the coarser size at a lower cut point, but this will divert coal to the reject stream and may not reduce the phosphorus by much in the clean coal. Some of the clean coarse-fraction coal, which contains the highest phosphorus concentration, could be diverted as a thermal product in which phosphorus content is not as much of a concern; the result would be a lower concentration in the metallurgical product.

CONCLUSIONS

It is proposed that much of the phosphorus in coal originates in the parent vegetation, in which there is ample to account for all that is found in coal. In fact, there may be more than enough and the problem is not one of how to get the phosphorus into coal, but one of how and where has it gone. It is suggested that the formation of inert macerals by the action of fires or bacteria in the pre-coal swamp environment produces a maceral with a robust and plentiful porosity. Shortly thereafter, the remaining vegetation goes through a gellification stage in an anaerobic, possibly acidic environment. During this stage, phosphorus is mobilized, largely from the vegetation, and redeposited in the cell porosity in the inert macerals. It forms minerals such as the calcium phosphate, apatite, the barium phosphate, goriexite and the strontium phosphate, goyazite. Many computerized x-ray diffraction systems will identify apatite, but the identification of the barium and strontium phosphates may be more difficult. This is important because, whereas x-ray diffraction work records the presence of apatite and gorciexite, oxide data implies that the phosphorus is often present as goyazite. Once redeposited in phyteral porosity in the inert macerals, the

phosphorus is difficult to liberate by conventional washing techniques.

Based on this, phosphorus content should correlate with the amount of inerts in adjacent samples from a single seam. The concentration in the inert macerals may be much higher than that in the reactive macerals or in ash bands. Because inherent ash also often resides in the phyteral porosity, there may be a correlation between phosphorus and ash, but this will not hold at higher ash concentrations when a larger component of the ash is derived from elsewhere. There will not necessarily be a correlation of phosphorus concentration with inerts content of samples from different seams because of the wide range of phosphorus concentrations in inerts. The phosphorus concentration of separate seams may correlate with vegetation type or other regional parameters.

Much of the phosphorus is present in phosphatic minerals in the coal and it may be possible to liberate and remove it during washing, as indicated by some seam data. However, it may be so finely dispersed in the phyteral porosity in inert macerals, that it will be difficult to remove. The best way of reducing phosphorus in clean coal may be by blending with ROM coal. This will require building good advanced knowledge of phosphorus concentrations in seams into long range mine plans.

ACKNOWLEDGMENTS

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