Trace element fractionation between PM$_{10}$ and PM$_{2.5}$ in coal mine dust: Implications for occupational respiratory health

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ABSTRACT

Investigations into the respiratory health impacts of coal mine particulate matter (PM) face the challenge of understanding its chemical complexity. This includes highly variable concentrations of trace metals and metalloids such as Fe, Ti, Mn, Zn, Ni, V, Cr, Cu, Pb, Cd, Sb, As and Sn, which may be capable of inducing cell damage. Analysis of PM$_{10}$ and PM$_{2.5}$ samples size-separated from deposited coal mine dusts collected on PVC flat surfaces at a height of 1.5-2 m inside the second level in the Velenje lignite mine, Slovenia, demonstrates that some of these metallic elements (in this case Cu, Sb, Sn, Pb, Zn, As, Ni) can be concentrated in PM$_{2.5}$, the most deeply inhalable and therefore potentially most bioreactive size fraction. These elements are likely to be mainly present in silicates, oxides, and perhaps antimonides and arsenides, rather than in the calcareous, carbonaceous or sulphide components which show no obvious affinity for PM$_{2.5}$. Whereas in the Velenje lignites concentrations of these metallic elements are low and so do not present any obvious extra health risk to the miners, this is unlikely to be the case in mines where unusually metal-enriched coals are being excavated. We therefore recommend that levels of potentially toxic elements in PM$_{2.5}$ should be assessed where metal- and metalloid-rich coals are being mined worldwide, especially given uncertainties relating to the efficiency of current dust suppression and respiratory protective equipment for such fine particle sizes.

1. Introduction

The recent resurgence of coal mine dust lung disease (CMDLD) has caught many in the scientific community by surprise. After several decades of substantial improvement in, for example, North American and Australian mines, coal miners are once again suffering in increasing numbers from coal workers' pneumoconiosis (CWP), a condition that can intensify into its most pernicious, incurable and potentially fatal form known as progressive massive fibrosis (PMF) (Johan-Essex et al., 2017; Perret et al., 2017). Medical surveys are further revealing that relatively young miners are being affected, even though they have spent their whole working lives to date under modern dust control regulations (Perret et al., 2017; Graber et al., 2017). Doctors and researchers who thought that the more serious forms of CMDLD belonged to the poorly regulated past have reacted with consternation: "It is unacceptable that new cases of pneumoconiosis should be occurring in the 21st century at a time when the knowledge regarding prevention of

such a disease is excellent. Lessons learned from the past seem to have been buried in the dusts of time" (Yates et al., 2016; see also Cohen et al., 2016). The pathology is reminiscent of the classic "U-shaped curve of concern" identified by Reichmann (1991) regarding the late 20th century return of tuberculosis (Petsonk et al., 2013). It is serious enough to warrant the status of an Occupational Sentinel Health Event (Rutstein et al., 1983; Antao et al., 2005), whereby the emergence (or, as in this case, re-emergence) of a preventable workplace disease provides a clear warning signal that new studies on the origin, control and prevention of the problem are required.

The key reasons for this epidemiological downturn in the health prospects of modern coal miners are as yet unclear and likely involve some combination of changes in mining targets, methods, and employment practices underground. There is evidence, for example, to indicate that miners working in smaller mines and spending longer hours specifically at the coalface are at enhanced risk of developing rapidly progressive CWP (Seaton et al., 1981; Kenny et al., 2002; Antao

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et al., 2005). Another consideration is that modern, commonly diesel-powered mining equipment, whilst more efficient at coal production, may create higher levels of PM underground, and that this dust may be different in character to that produced by more traditional mining methods (Petsonk et al., 2013). Comparisons between ambient coal mine dust produced in the 1920's and that produced this century, for example, suggest that the airborne particulate matter (PM) underground has become finer with time (Sapko et al., 2007). A complicating factor is the observation that the specific nature of new CMDLD cases seems to vary between regions and countries, for example between traditional CWP or more silicosis-like patterns (e.g Blackley et al., 2018; Cohen et al., 2016).

The current situation described above also revives old arguments about whether CMDLD risk is primarily simply a question of dust concentration and length of exposure (combined with influencing factors such as smoking habits and genetic predisposition), or whether the mineralogy and geochemistry of the PM being inhaled are additional factors. In this context the inability of research workers to identify a clear inorganic "smoking gun", in the form of a specific mineral that can be proven to induce CWP, has generated uncertainty. For example, although regulations have focused on respirable quartz, which is primarily responsible for silicosis and capable of inducing pulmonary fibrosis (NIOSH, 2002), doubt remains as to whether this mineral is also a major influence on CWP (Lapp and Castranova, 1993; Beer et al., 2017). Thus CWP has been positively correlated with coal rank (Attfield and Morring, 1992) but negatively correlated with quartz content (Harrison et al., 1997); some authors have concluded that "quartz is not the predominant factor in the development of CWP" (Mccunney et al., 2009). Changing work practices underground, however, such as the mining of thinner coal seams with the consequent release of siliceous dust from adjacent rocks, may be inducing symptoms more allied to silicosis than "traditional" CWP, adding further confusion to the evaluation of newly emerging disease patterns (Cohen et al., 2016).

It is clearly not enough to focus entirely on specific minerals such as quartz, or other components, as a generic causative agent of negative health effects induced by coal mine dust, especially given the chemical complexity of particulate materials potentially inhaled in mines. Whereas coal mine dust typically has a simple inorganic mineralogy dominated by silica (mostly quartz), phyllosilicates (mostly illite, kaolinite and/or montmorillonite), carbonates (typically siderite, ankerite and calcite) and sulphides (mostly pyrite) (Riley et al., 2012), it has a much more complex organic and trace element geochemistry. Of relevance here is the fact that both the organic (macerals) and inorganic (mineral) components of coal mine dust house a wide range of metallic elements known to be potentially capable of inducing cell damage after inhalation. Such elements may accumulate within the millimetric-sized dark carbonaceous dust-rich lesions known as "macules" that characteristically develop around the respiratory bronchioles of coal miners with CWP. Some researchers have already implicated transition metals such as bioavailable Fe or Ni to be significant influences on the incidence of CWP (Christian et al., 1979; Huang et al., 2002; Mccunney et al., 2009; Harrington et al., 2012), but there remains in general a lack of information about the exact character of the materials being inhaled in the mine dust because most papers dealing with coal trace element geochemistry focus on toxic emissions and wastes produced during combustion. In this paper therefore we refocus on the PM breathed by miners, identifying the main metallic elements likely to be of concern in these coal mine dusts, and presenting an exploratory pilot case study that demonstrates how dust chemistry, and especially metal and metalloid contents, can change as particle size decreases and the materials become more deeply inhalable.

2. Metallic elements of potential concern in coal mine dust

The inflammatory mechanisms likely involved in CWP are well documented and will not be repeated in detail here (see for example the review by Schins and Borm, 1999). Essentially, the deposition of abundant coal mine dust particles deep in the lung encourages the overproduction of reactive oxygen species (ROS) and other compounds that challenge and can overwhelm the antioxidant defence systems of cells. The coal mine dust can be directly cytotoxic, especially if particles are rich in bioreactive surface radicals, but it can also induce cell damage indirectly by activating alveolar macrophages to release ROS and proteins that escalate the inflammation around the macule site. The process will be facilitated by the presence of redox-active metals such as Fe, Mn, Cu, V and Cr which contribute to ROS production via Fenton-type reactions, although even redox-inactive metallic elements such as Pb, Cd, Hg and As can also produce ROS by acting directly on cellular molecules (Ercal et al., 2001; Birben et al., 2012; Valko et al., 2016; Ghio and Madden, 2017).

We identify a shortlist of metallic elements of potential concern in coal mine dust with respect to CWP, all of which have been shown to be capable of involvement in ROS production and cell damage. The concentration hierarchy of these metallic elements in world coals (Ketris and Yudovich, 2009) using arithmetic means is as follows: Fe (< 50,000 ppm), Ti (< 1,000 ppm), Mn (< 100 ppm), Zn, V (< 50 ppm), Ni, Cr, Cu (< 20 ppm), Pb, As, Se, Sb and Sn (< 10 ppm). These average concentrations obscure wide regional variations in coal geochemistry so that mean Cr contents for Chinese coals (32 ppm), for example, are much richer than for "world coals" (Yan et al., 2014). Furthermore, at a local level certain elements can become unusually enriched, with metal concentrations in some coals reaching > 14 wt% Fe, > 1.5 wt% Zn, > 8,000 ppm Mn, > 2,000 ppm As, > 1,900 ppm Pb, > 1,400 ppm V, > 900 ppm Cr, and > 300 ppm Ni and Cu (Dai et al., 2012). The "top ten" metallic elements ranked broadly in terms of their average concentrations in coal-derived mine dusts are therefore Fe, Ti, Mn, V, Zn, Cr, Cu, Ni, Pb and As. The occurrence modes of each of these metallic elements in coal-derived mine dust is briefly summarized below.

Iron is ubiquitously present in coal mine dust although its concentration varies greatly between different coals. It occurs in silicate (e.g. clay minerals), carbonate (e.g. siderite and ankerite), sulphide (e.g. pyrite) and sulphate particles, as well as bound to the coal macerals (Finkelman et al., 2018). Pyrite and marcasite are the commonest ferruginous sulphide minerals in coal and typically contains As, Cu, Ni, Co and Pb at concentrations of 100-1000 ppm, as well as a range of other trace elements such as Mo, Zn, Sb, and Se at lower concentrations (Kolker, 2012; Gregory et al., 2015). These trace elements may be concentrated within embedded microinclusions (such as is commonly the case with Zn and Cd in tiny sphalerite crystals) or be distributed more evenly through the pyrite structure (more typical, for example, of As: Gregory et al., 2015). Ferruginous particles can be biopersistent: it has been calculated that an inhaled 1 μm-sized pyrite crystal is likely to remain in the lung for over a year as it slowly dissolves, promoting the formation of ROS within cells and potentially contributing to the pathogenesis of CWP (Harrington et al., 2012). In addition, some of the iron in coal mine dust will be present in bioavailable forms within the carbonaceous humic substances that have also been signalled as likely involved in ROS generation and cell damage (Ghio and Quigley, 1994). A strong case has been made for bioavailable iron (BAI) to be closely linked to CWP pathology, more so than quartz or coal rank (Huang et al., 2002, 2005).

Titanium is the second most abundant transition metal in coals and occurs both in tetravalent isomorphous substitution for silicon in quartz as well as in oxide form (Rakov, 2006). Inhalable-sized microcrystals of the oxides rutile and anatase (TiO_2) of detrital origin are commonly visible embedded in coal mine dust clays and organic materials (Steinmetz et al., 1988). Titanium can also be sorbed onto clay minerals such as kaolinite (and also probably illite) or occur as fine-grained anatase within the kaolinite (Dai et al., 2015), or can occur in sulphides such as pyrite, and may be present to a limited extent in the organic fraction (Finkelman et al., 2018). Titanium oxides are relatively

chemically inert and poorly soluble, and so would be expected to be biopersistent in the lung environment. Involvement of such particles in ROS generation and cell damage is more likely to be due to their physical form rather than chemistry. In this context, for example, there is increasing concern over anthropogenic TiO_2 nanoparticle toxicity, especially when such particles possess shapes (such as highly elongated) that phagocytic cells have difficulty in processing (Hamilton et al., 2009).

Manganese in coal mine dust usually occurs in carbonates (substituting for Fe in ankerite and siderite), but it can also be found in trace amounts within clay minerals, sulphides, oxides and in the organic fraction (Finkelman et al., 1994; 2018). Manganese inhaled in unusually high concentrations is known to be toxic (Moreno et al., 2011), although given Mn concentrations typical of most coals (< 100 ppm: Finkelman et al., 2018) within the underground mine environment, any risk associated with Mn inhalation is likely to be very low.

Zinc and cadmium in coal most commonly occur in sphalerite (ZnS), although they can also be associated with clay minerals (notably illite) or present in oxide form (Finkelman et al., 2018). Coals that are unusually enriched in Zn typically contain sphalerite precipitated from zinc-bearing brines under sulphur-rich reducing conditions during coalification (Swaine, 1994). The sphalerite, which commonly contains trace amounts of Cd and Se, can occur associated with pyrite as well as with galena in mineralised veins and cleats (joints). Although Zn is known to be capable of involvement in ROS generation and cytotoxicity, especially in nanoparticulate form (e.g. Fu et al., 2014), it is unlikely that significant amounts of bioavailable Zn are inhaled by coal miners in a mine lacking abnormal concentrations of this metal. However, note that where high levels of Zn do occur then elevated levels of Cd are also likely in ambient dust.

Nickel in coals is likely to reside mostly in the sulphides and bound to organic compounds, although the metal also shows affinities with selenides, antimonides and arsenides (Finkelman et al., 2018). Nickel can thus occur as discrete minerals such as millerite (NiS), linnaeite ((CoNi)$_3$S$_4$), ullmannite (NiSbS), and clausthalite (PbSe), or as substitutions and microcrystals in sulphides (such as galena, sphalerite, and pyrite) and silicates (notably adsorbed to clay minerals) (Hower and Robertson, 2003; Dai et al., 2015b). As described above for zinc, nickel has been shown to be capable of ROS generation and cytotoxicity, although interestingly there is evidence to suggest that micron-sized rather than nanometric Ni PM are more bioreactive (Latvala et al., 2016).

Vanadium in coals is associated with both inorganic (mostly phyllosilicates, especially at higher coal ranks) and organic materials (especially at lower coal ranks such as lignite) (Liu et al., 2016). Although on average V is depleted in coals with respect to continental crust, striking exceptions occur across large parts of Southern China where concentrations of this metal can reach 8,000 ppm in Palaeozoic carbonaceous shales known as "stone coals" (Jiang et al., 1994), or in coals derived from the Kangdian Upland mafic sediment source region (Dai et al., 2014). The V enrichment is typically accompanied by significant enhancements in Mo, Ni, U, P, Cd, as well as enhanced levels of Au, Ag, Cu, Co, Zn, Se, Ga, Ge, Sc, Ti, REE, and Y (Dai et al., 2018). These coals have resulted from a combination of a chemically distinctive sediment source (e.g. erosion of V-enriched basalts) with a sulphurous black shale depositional environment concentrating V under anoxic conditions (Liu et al., 2016). In some areas the V enrichments have been enhanced by hydrothermal fluids that can result in the crystallisation of vanadinite (Pb$_5$(VO$_4$)$_3$Cl), but V usually occurs as organic matter and, to a lesser extent, associated with clay minerals (Liu et al., 2015; Dai et al., 2008). Although V is toxic when inhaled at high concentrations (WHO, 2000), it is not considered to be a metallic element of concern to most miners. It is likely, however, that this conclusion does not apply in the exceptional case of the Chinese V-rich stone coal mines, this being especially relevant given the increasing interest in expanding the exploitation of this important strategic resource.

Chromium in coal mine dust is likely to be mostly bound to organics as well as associated with silicates (notably in phyllosilicates such as illite), with lesser amounts occurring within sulphides, carbonates and oxides (Liu et al., 2015; Dai et al., 2008; Finkelman et al., 2018). This metal may also be present in microcrystals of chemically resistant minerals such as spinel, corundum, beryl and tourmaline; coals exceptionally enriched in Cr (> 500 ppm) can display crystals of chromite (FeCr$_2$O$_4$). Available evidence indicates that Cr in coal is present in the trivalent (Finkelman et al., 2018) rather than the much more toxic hexavalent form which is a known lung carcinogen. Although pneumoconiosis and cancer has been documented from the lungs of chromium mineral workers (WHO, 2000), we are not aware of any evidence to suggest that this metal represents a significant health threat to coal miners.

Copper in coals is distributed between the sulphide, selenide, carbonate, silicate and organic fractions (Riley et al., 2012; Dai et al., 2015; Finkelman et al., 2018). Crystals of chalcopyrite, commonly associated with galena, can be found filling voids within coalified peat (Finkelman et al., 2018). In exceptional cases, coal can contain > 400 ppm Cu, although average levels in coal are < 20 ppm making this metal unlikely to accumulate to high concentration levels in the total suspended particulate loading typical of the coal mine atmosphere.

Lead is primarily present in coals as galena (PbS), although it can also be found as the selenide clausthalite (PbSe) which occurs in solid solution with the sulphide (Hower and Robertson, 2003; Dai et al., 2006). Galena can occur commonly with other sulphides as relatively large epigenetic crystals filling fractures in the coal, but also as microcrystals inside pyrite and disseminated within the organic materials (Swaine, 1994; (Finkelman et al., 2018)). Although a well-documented neurological toxin, lead is normally present in very low levels within coal-bearing strata unless there has been significant late mineralisation.

Arsenic is widely distributed in coals, variously occurring in sulphides, silicates (mostly clays: kaolinite, smectite, illite), phosphates, carbonates, sulphates and arsenates, as well as organically bound. It is a common (up to 10 wt%) substitute for Fe in both finely dispersed syngenetic pyrite and epigenetic pyrite veins and cleats, and can occur as arsenopyrite (FeAsS), although Finkelman (1994) has correctly argued that this occurrence has been exaggerated. Whereas the As content of most coals is low (World Average 9 ppm: Ketris and Yudovich, 2009) and poses no obvious risk to coal miners, some deposits are spectacularly As-rich (such as the 35,000 ppm As-bearing coal reported from Guizhou Province in China by Finkelman et al., 2002). As with V, these natural As enrichments typically owe their origin to some combination of distinctive sediment source and later hydrothermal fluid movement. Most notorious are coals in parts of China, for example around Guizhou, where As poisoning due to domestic coal combustion is well documented (Belkin et al., 2008; Tian et al., 2013; and references therein). The effects of inhaling dust from the mines sourcing these coals does not appear to have been investigated, although a link between lung cancer and As inhalation in hard rock mines has been demonstrated (Taylor et al., 1989). The extreme toxicity of inorganic As and its proven role in ROS production and carcinogenesis within the lung (WHO, 2000) provides obvious cause for concern for miners working with high-As coals.

3. Pilot study: fractionation of metallic elements in Velenje mine coal dust

3.1. Methods

Given the overview presented above, we now consider the presence and distribution of metallic elements in coal mine dust in the light of the recently launched European ROCD Project (*Reducing risks from Occupational exposure to Coal Dust, 2017–2020*) which has reopened investigation into the mineralogical and chemical composition of airborne particles in underground coal mines. Part of the work schedule
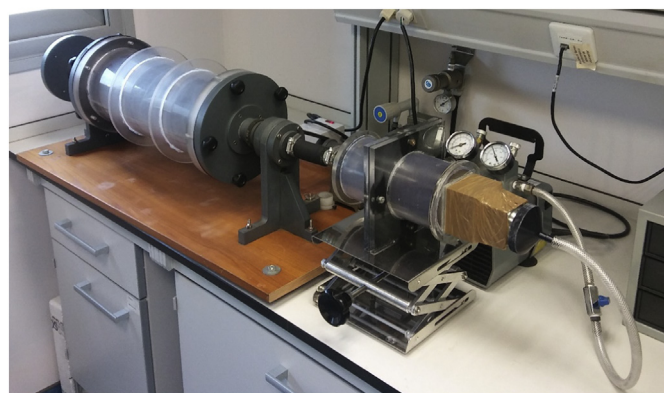
Fig. 1. Rotating cylinder device used to separate the inhalable particulate matter present in coal dust. TDS: Total Deposited Sample, PM: Particulate Matter.

for this project is to obtain a large chemical database on coal mine dusts separated into different size fractions. In order to achieve this, a protocol has been developed to allow the separation and comprehensive chemical analysis of inhalable and respirable PM fractions from coal dust collected inside mines. The method uses a specially designed and patented (Patent No. 201131895) particle size separation device (Fig. 1) comprising a rotating 17 cm diameter methacrylate cylinder which is attached at one end to a filter sampling head through which air is drawn by a pump. The cylinder is continuously rotated to resuspend PM which is then collected on a 0.60 μm pore size polycarbonate filter, at an air flow rate of $25\,l\,min^{-1}$ or $5\,l\,min^{-1}$ to collect PM_{10} and $PM_{2.5}$, respectively. Two hundred grams of each total deposited particle (TDP) sample collected in the Velenje mine were introduced in the cylinder in order to obtain 1.7 and 1.6 g of PM_{10} and $PM_{2.5}$ respectively for each sample after 8 and 32 h rotating for PM_{10} and $PM_{2.5}$ samples respectively. Approximately 0.1 g of each sample were used for chemical analysis.

Chemical analysis of the PM_{10} and $PM_{2.5}$ samples involves using ICP-MS and ICP-AES, using a two-step acid digestion method devised to retain volatile elements (Querol et al., 1997). In order to obtain detailed (low detection limit), accurate and precise major and trace element data for coal dust samples we applied a tried-and-tested standard acid digestion technique involving the use of 60 ml PFA bombs. The method is summarized as follows: 2.5 ml of concentrated MERC supra-pure nitric acid (65%) is added to 0.1 g of coal sample and heated to 90 °C in a closed bomb for 4 h. After water addition (MilliQ, 18.2 MI∼ − cm), the mixture is centrifuged and the solution obtained transferred to a volumetric flask (100 ml). The residue is water washed and centrifuged twice before adding the washing solution to the graduated flask. The residue is then transferred to the PFA bomb again and 7.5 ml of MERC supra-pure hydrofluoric acid (40%) and 2.5 ml of concentrated MERC supra-pure nitric acid (65%) added; the closed bomb is heated at 90 °C for 4 h 2.5 ml of MERC supra-pure perchloric acid (60%) is added and the mixture then heated at 250 °C to dryness. After that, when the sample is dry, add 1 ml of MERC supra-pure nitric acid (65%) to fix the sample and wait for it to evaporate. Once total dryness is reached, 2.5 ml of MERC supra-pure nitric acid (65%) is added and the solution transferred to a graduated flask (with the solutions obtained from the first stage) to make a volume of 100 ml. The final acid concentration is 2.5% nitric acid. The resulting solutions are then analysed by inductively-coupled plasma atomic-emission spectrometry (ICP-AES) for major and selected trace elements and by inductively-coupled plasma

mass spectrometry (ICP-MS) for most trace elements. In order to check accuracy, the international coal reference material (SARM-19) and blanks were digested and analysed following the same procedure. Analytical errors were estimated at < 3% for most of the elements and around 10% for Cd, Mo, and P.

3.2. Regional setting

We applied this ROCD extraction-and-analysis protocol to samples of deposited coal dust collected inside the underground Velenje lignite coal mine located in the Šaleška valley, Slovenia. The Velenje Coal Mine is one of the largest and most modern deep coal mining sites in Europe operating on the largest Slovenian coal deposit and on one of the thickest known coal layers in the world (Markič, 2009; Markič and Sachsenhofer, 2010). The mining method used is known as Velenje Mining Method (VMM). The coal seam is 8.3 km long and up to 2.5 km wide at a depth between 200 and 500 m. Its average thickness is 60 m, with maximum values reaching up to 170 m. The area of exploitation extends above a hydraulic shield support which dynamic stresses cause breaking and crushing of the coal in upper excavation section (without blasting). In the lower excavation part, 3-4 m high protected with hydraulic shield support, the extraction of coal is achieved using a shearer. The mine ventilation system consists of over 60 km of roadways and other structures, with two surface ventilation stations exiting mine air, with total continuous airflow between 21,000 m^3/min and 25,000 m^3/min (Uranjek et al., 2013).

3.3. Results

The total deposited particle (TDP) samples obtained from the Velenje mine comprised ambient airborne dust collected passively over 24 h on PVC flat surfaces located at a height of 1.5-2 m inside the second mine level 20 m away from the longwall air outlet at the time excavation was taking place. Samples were collected from the same place using a brush (sample ROCD_1) or (three months later) a metal rule (sample ROCD_2) to scrape the sample into PVC sample pot, and then sent to Barcelona for size fractionation and analysis. The use of the metal tool for the ROCD_2 sample collection did not produce any obvious metallic contamination in the dust sample (as observed in the chemical results). The results from this pilot study provide a concise demonstration of how the metallic content of coal mine dust can change as the dust becomes finer and more deeply inhalable.

Table 1 presents results from the analysis of TDP samples collected in the underground Velenje mine and of PM_{10} and $PM_{2.5}$ separated from them. Results are shown as dry basis given the fact that the sample moisture is likely to change during transport and sample processing in the laboratory (in our case from 19 to 20 wt% at the sampling site to 10–13 wt% in the laboratory). In terms of major elements, all samples demonstrate their similar source by showing broad chemical similarities, with Ca, Al and Fe together comprising around 10 wt% of the particle mass, sulphur having values of 1.5-3 wt%, and Mg, K, and Na comprising 1-2 wt%. However, there are clear differences between TDP and the finer fractions (Fig. 2). In the coarser TDP, Ca is the most common cation but decreases in concentration in the finer fractions and can be overtaken in mass by Al which consistently increases from TDP through PM_{10} to $PM_{2.5}$. Most of the other major elements exhibit a similar behaviour to Al, with Fe, Mg, and especially K and Na all attaining highest levels in the $PM_{2.5}$. SEM-EDS analysis of the samples suggests that the main source of S in the samples is in the form of pyrite particles, and X-ray diffraction of the samples confirms the presence of quartz, illite, pyrite, calcite, and gypsum. Although we do not have analyses of the parent lignites directly sourcing our dust samples, Table 1 includes a column showing average compositions of 24 Velenje lignite borehole samples analysed by Markič (2009). The average lignite and our TDP samples show similar C and S concentrations, but all other elements analysed have higher concentrations in the TDP samples

Table 1

Major and trace element concentrations determined by ICP-AES and MS. TDP = Total Deposited Particulate (i.e. passively deposited coal mine dust). Moisture (M), Ash content (HTA) and % concentrations of C, N, and H. ar = as received basis, db = dry basis. Velenje lignite data recalculated from Markič (2009): average of 24 ICP-AES and ICP-MS analyses from successive samples 95CK to 43CK obtained in vertical structural borehole P-9 k/92 (drilled perpendicularly from the seam roof to a depth of 81 m).

	Unit	Velenje lignite	ROCD_1			ROCD_2		
			TDP	PM_{10}	$PM_{2.5}$	TDP	PM_{10}	$PM_{2.5}$
M	%ar		13.26	1.62	1.36	10.06	2.82	2.78
HTA	%db		33.79	34.23	37.94	29.67	31.06	32.65
C	%db	44.98	43.08	40.89	37.85	46.54	43.00	41.18
N	%db		0.91	0.82	0.80	1.08	0.99	0.99
H	%db		3.98	3.27	3.10	3.94	3.49	3.32
Al	%db	1.72	3.39	3.58	3.90	2.70	2.78	3.11
Ca	%db	2.56	4.14	3.64	3.70	4.25	3.74	3.85
Fe	%db	1.66	3.16	3.24	3.60	2.68	3.15	3.24
K	%db	0.27	0.63	0.75	0.84	0.50	0.58	0.64
Mg	%db	0.27	0.56	0.57	0.61	0.47	0.48	0.51
Na	%db	0.10	0.27	0.34	0.37	0.23	0.28	0.31
P	%db	0.03	0.06	0.06	0.07	0.05	0.06	0.06
S	%db	2.28	2.51	2.36	2.41	2.84	2.65	2.88
Li	mg/kg db		14	15	17	10	10	12
Be	mg/kg db		0.7	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sc	mg/kg db		4.7	4.5	4.8	2.9	< 0.1	2.9
Ti	mg/kg db	640	1191	1175	1291	875	961	953
V	mg/kg db	28	47	44	57	36	38	42
Cr	mg/kg db		32	35	42	23	31	34
Mn	mg/kg db	542	724	707	730	790	849	833
Co	mg/kg db	2.6	4.7	5.9	6.6	3.4	5.8	5.8
Ni	mg/kg db	8.6	19	30	32	17	30	42
Cu	mg/kg db	8.6	17	35	44	14	31	65
Zn	mg/kg db	22	69	119	139	55	103	125
Ga	mg/kg db	4.6	6.7	8.2	9.5	4.8	6.4	7.3
Ge	mg/kg db		< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
As	mg/kg db	8.2	13	19	25	10	19	20
Rb	mg/kg db	21	38	46	51	28	37	38
Sr	mg/kg db	94	137	131	139	110	112	117
Y	mg/kg db	5.8	8.9	8.9	9.4	6.5	6.6	7.4
Zr	mg/kg db	16	25	26	26	18	16	20
Nb	mg/kg db	1.8	4.7	4.6	5.1	3.3	2.7	3.5
Mo	mg/kg db	10	22	25	27	20	16	26
Cd	mg/kg db	0.2	< 0.1	< 0.1	< 0.1	< 0.1	0.5	< 0.1
Sn	mg/kg db	1.2	1.5	3.5	5.1	1.1	2.4	5.0
Sb	mg/kg db	0.4	2.0	5.8	7.0	1.5	5.7	6.2
Cs	mg/kg db	2.1	3.6	4.5	5.1	2.5	3.7	3.5
Ba	mg/kg db	78	154	172	195	115	144	146
La	mg/kg db	6.9	12	12	13	8.8	10	10
Ce	mg/kg db	12	21	21	24	16	20	19
Pr	mg/kg db	1.5	2.6	2.7	3.0	1.9	2.4	2.3
Nd	mg/kg db	6.6	9.8	10	11	7.4	8.8	9.0
Sm	mg/kg db	1.2	2.0	2.1	2.3	1.5	1.8	1.7
Gd	mg/kg db	1.1	1.8	1.7	2.0	1.3	1.6	1.4
Dy	mg/kg db	0.9	1.6	1.6	1.7	1.2	1.4	1.3
Er	mg/kg db	0.5	0.8	0.8	0.9	< 0.1	< 0.1	< 0.1
W	mg/kg db	0.6	0.8	1.1	1.4	< 0.1	0.9	0.9
Pb	mg/kg db	8.7	16	28	35	13	42	33
Bi	mg/kg db	0.2	< 0.1	< 0.1	< 0.1	< 0.1	0.2	< 0.1
Th	mg/kg db	2.5	3.7	3.9	4.3	2.8	3.1	3.3
U	mg/kg db	9.5	13	14	15	10	9.2	12

(commonly 2 or 3 times higher), suggesting the trace element fractionation observed in the inhalable dusts has also operated in the initial release of PM during mining of the parent coals.

This preference for the finer dust fractions is also demonstrated by many of the trace elements presented in Table 1. The concentration hierarchy of trace elements in the TDP samples from highest to lowest is as follows: Ba, Sr, Zn, V, Rb, Cr, Zr, Ni, Cu, Mo, Pb, Li, U, As, La, Y, Ga, Sc, Co, Nb, Th, Cs, Pr, Sm, Sb, Gd, Dy and Sn. However, in the PM_{10} and even more so in $PM_{2.5}$ samples extracted from the TDP samples, this hierarchy is disrupted by several elements leapfrogging to higher positions. Those elements showing the least tendency to concentrate in the finer fractions are Sr, Zr, Y, Sc, Nb, Sm, Gd, and Dy. In contrast Ba, V, Rb, Cr, Mo, Li, Ga, Co, and Cs all increase moderately from TDP to $PM_{2.5}$. The most extreme preferences for the finer PM fraction however

are exhibited by Zn, Ni, Pb, As, and especially by Cu, Sb and Sn (Fig. 3). In most cases these seven metallic elements more than double in concentration from TDP to $PM_{2.5}$ (Table 1).

4. Discussion and conclusions

The lignites mined at Velenje lie within the normal range of chemical compositions for coal worldwide (Ketris and Yudovich, 2009; Swaine, 1990, Fig. 4) and do not stand out as being exceptionally enriched in any element except Mn (compare for example Markič, 2009 with Yan et al., 2014). It is all the more interesting therefore that such a chemically unexceptional lignite shows significant enrichments of metallic elements in the more deeply inhalable fraction of coal dust present in the mine air. It is well established that many metallic particles
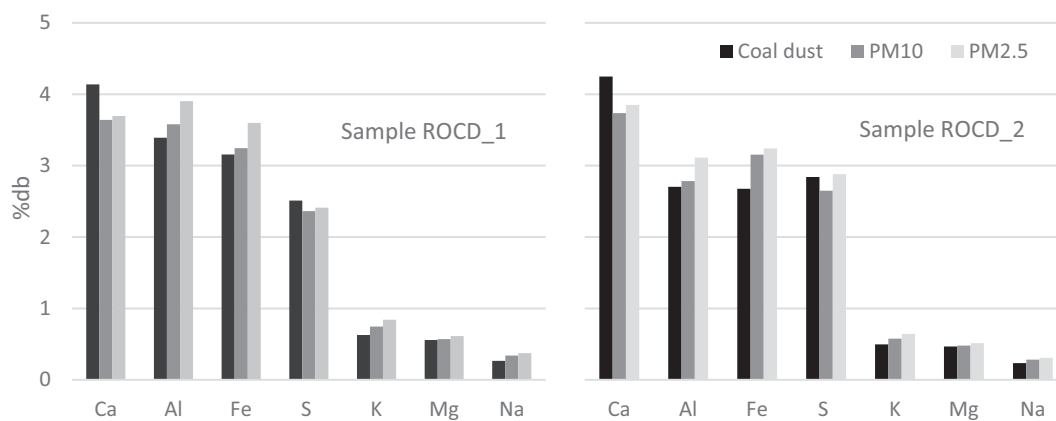
Fig. 2. Concentrations of principal major elements in the TDP (coal mine dust), PM_{10} and $PM_{2.5}$ fractions of the samples analysed.
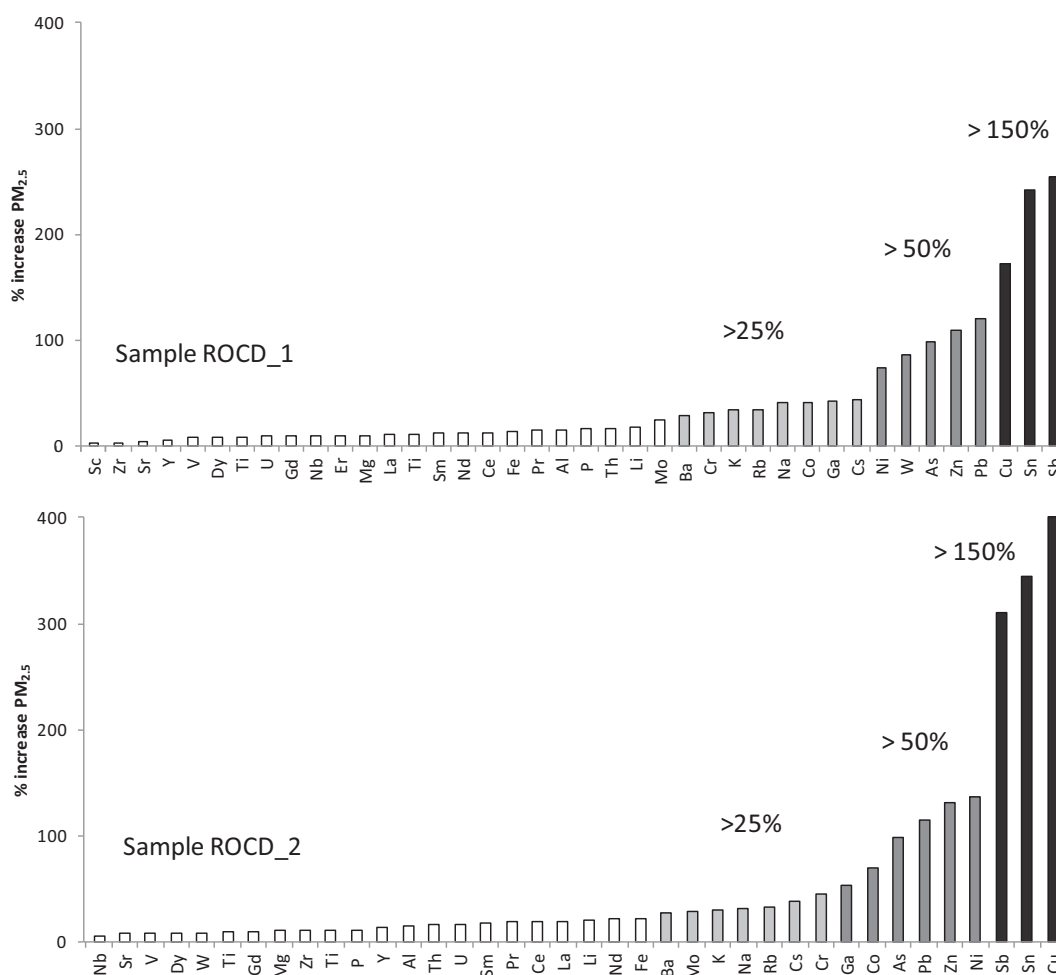

Fig. 3. Percentage enrichment in different elements between $PM_{2.5}$ and TDP.

tend to fractionate into fine size fractions ($PM_{2.5}$, and ultrafine), whereas mineral particles are coarser and predominate in the PM_{10} fraction (Williams et al., 1994; Moreno et al., 2006; NIOSH, 2010; Kollipara et al., 2014). At Velenje, for example, Cu concentrations in lignites with > 45% carbon average below 10 ppm (Markič, 2009), which is well below world average levels (Yan et al., 2014). Given our observation that $CuPM_{2.5}$ concentration extracted from the Velenje TDP samples can reach 65 ppm, with $PM_{2.5}$/TDP increasing by > 400%, there exists the possibility for extremely high Cu-PM concentrations in the ambient air of mines excavating unusually Cu-rich coals, such as the

Jungar coalfield of inner Mongolia, Northwestern China where individual coal seams can average 55 ppm Cu (Liu et al., 2018).

A similar argument applies to the other six metallic elements identified in our study as capable of strong enrichment in the inhalable fraction of coal mine dust, namely Sb, Sn, Pb, Zn, As and Ni. In the case of Sb, for example, enrichments measured in $PM_{2.5}$ samples are seven times higher than the average levels reported from the parent lignite (Markič, 2009). Either an additional source of this element is contributing to the ambient $PM_{2.5}$, or much of the Sb in the lignite is present in very fine particles (Dai et al., 2015). In the case of Velenje,
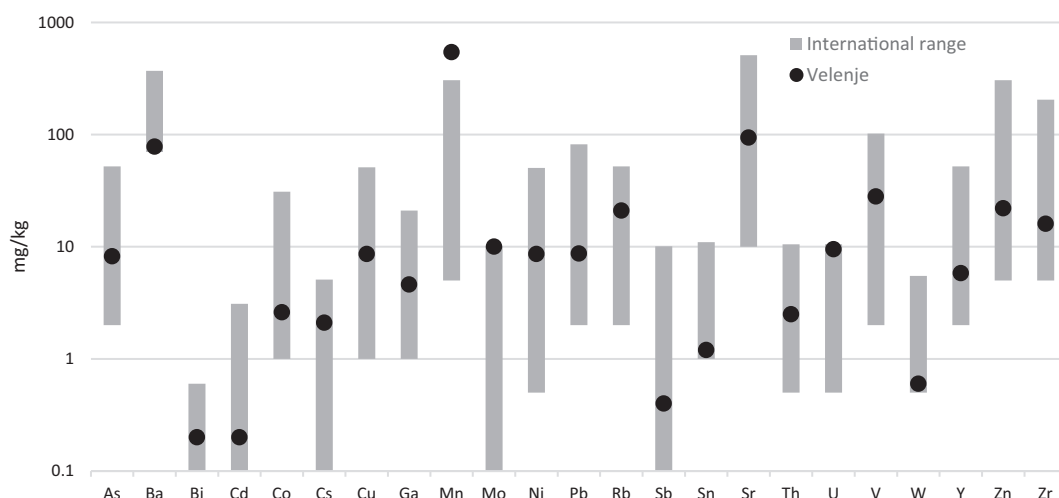
Fig. 4. Comparison of trace element Velenje coal composition with the coal world range from Swaine (1990).

the low levels (just 7 ppm Sb-$PM_{2.5}$) are of little concern, but some mines extract coal extremely enriched in Sb associated with the activity of carlin-type ore-forming fluids (Dai et al., 2012). It would be of interest to know ambient inhalable SbPM concentrations in coal mine dust from, for example, the Gokler Coalfield of western Turkey where coals contain on average 134 ppm Sb (and 833 ppm As: Karayigita et al., 2000), or the anthracites from Xingren, Guizhou, Southwest China, recorded as containing up to 3860 ppm Sb and 2226 ppm As (Dai et al., 2006).

Comparison of Ca and C concentrations in the TDP and extracted PM fractions indicate that in the Velenje mine at least it is not the calcareous or carbonaceous components of the airborne coal mine dust that are concentrating in the most inhalable particles (Table 1). Instead, the increasing levels of the cations Al, Fe, Mg, K and Na suggest the presence of fine silicate particles and oxides (and perhaps antimonides and arsenides) in the $PM_{2.5}$, rather than carbonates. This conclusion offers a hypothesis that can be tested by using other analytical methods such as scanning electron microscopy and invites a closer characterisation of the particulate matter forming these coal mine dusts.

We realise that other possible sources of particulates can contaminate passively collected coal mine dust samples, such as PM generated by machines cutting the coal strata, and especially by the involvement of siliciclastic sediments interlayered with the carbonaceous deposits. However, in our case the Velenje lignite was selected for its unusual thickness and relative chemical homogeneity (Table 1), and no diesel equipment is used in the mining operations that could emit metals in the $PM_{2.5}$ fraction. However, a limestone dusting product is applied to mitigate explosion hazards, and this could be influencing the different fractionating behaviour shown by Ca compared to other major cations.

Finally, we return to the initial topic of this paper, that of coal miner health. In this paper we identify seven metallic elements that, in our study at least, can become strongly concentrated into the finer, more inhalable fraction of airborne coal mine dust. These metals and metalloids are Cu, Sb, Sn, Pb, Zn, As and Ni. All of these metallic elements are known to be capable of inducing negative health effects in humans and therefore are of concern in situations where they become unusually concentrated. In the case of the Velenje coal mine, their concentrations are very low in the parent coal (compared with coals worldwide) and therefore are not excessively present in the ambient air. However, it is well known that coal is chemically extremely complex and highly variable in composition. Published concentrations of these seven elements in coals worldwide can reach hundreds and, in the case of Zn, Mn, As and Sb, thousands of ppm. We predict from our study of the Velenje lignite dust that the inhalable content of these seven metallic

elements in coal mine air may be much higher than concentrations measured in TDP passive aerosol samplers, and very much higher than in analyses of the parent coals. Future research considering the possible health effects of coal mine dust would do well to focus specifically on the fine, inhalable fraction as our study demonstrates that this is chemically very different from the coarser airborne materials present in mine air.

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