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Fate and Transport of Fire-Born Particles in Porous Media

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Abstract: A variety of hazardous substances may be generated from the burning materials during fire extinguishing operations, depending on the location, type, and place of the fire. As a result, the fire-extinguishing water may act as a carrier for these nano- and micro-sized fire-born particles, including various types of associated contaminants, and may cause contamination of soil and groundwater resources. While airborne particles from fires have been studied, it is currently not well known what types of nano- and micro-sized contaminants are typically carried by the fire-extinguishing water and how these contaminants can be transported in the natural environment. The main purpose of this study was to increase the understanding about the occurrence and physical and chemical properties of nanoparticles commonly found in discharge water from fire extinguishing operations. The current study was based on collection of original samples from a fire location. A detailed characterization of the particles present in the extinguishing water was performed including both quantification of contaminants associated with the particles (such as metals and polycyclic aromatic hydrocarbons (PAHs) as well as measurement of properties related to the mobility of these particles through porous media. Such mobility properties include size distributions of the particles and the porous media, surface charges and solution chemistry). Results indicate that metals and PAHs are present in both finer and relatively larger fire-born particles. The particles larger than 11 μm were not mobile in porous media. The mobility of the finer particles ($<11 \mu\text{m}$) was generally high but was dependent on the solution chemistry. Low mobility of large particles in porous media indicates that a large amount of the contamination can likely be trapped in the top soil layer even though the fire extinguishing water infiltrates.

Keywords: fire particles; carbon; transport; retention; straining; porous media

1. Introduction

Fires in buildings such as households, and industrial or municipal buildings are common worldwide e.g., more than 10,000 fires in buildings were reported in Sweden alone in 2012 [1], and, in about 40% of these events, the fire was extinguished by the rescue services agencies. In most fire events, water is used as an extinguishing agent. Depending on the type of fire, the burning material and extinguishing method *etc.*, a variety of toxic compounds and particles can be formed. The particles (fire-born particles, FBPs) and associated contaminants can contaminate the extinguishing water. If this water is not collected on-site and disposed of safely, the contaminants carried with it infiltrate soil and groundwater systems or spread in the storm water system.

Anticipating the contamination content in the extinguishing water is a complex process because many factors affect the concentration of contamination and particles. Three different types of sources can contribute to pollution in a fire event: (i) material burning, (ii) items at the fire scene which

were not affected by the fire but were transported from the scene with the extinguishing water, and (iii) additives to the extinguishing water used for firefighting [2]. Pollution contributions from the first two sources vary widely and the chemical and particulate composition of the extinguishing water thus becomes unique to each individual fire. However, the contribution from the third source can likely be present at all fire locations.

Particle generation in fires is dependent on the burning material and combustion conditions where oxygen supply and temperature are important factors. Air supply and fire intensity can affect combustion rate and thus the compound formed from the burning material. For example, a well-ventilated fire with high combustion rate can generate a lower concentration of pollutants in the extinguishing water than an incomplete combustion of fire material [3]. Part of the particles contained in the fire extinguishing water comes from material, which has not undergone complete combustion or condensed substances after cooling of flue gas or formed by incomplete chemical reaction [4]. If the compound in the gas phase condenses when flue gas is cooled down, the enrichment of pollutants on the particles can be larger [5]. Usually, soot is present in a large amount of particles from a fire and can be formed under reducing conditions of incomplete combustion generating polycyclic aromatic hydrocarbons (PAHs) [4].

As particle formation in runoff water after any fire event depends on specific conditions and fire locations, it may be difficult to create a general understanding of their content [6]. However, there are a number of studies of particle formation in the air during the combustion of various materials and material mixtures (such as [7,8]). In these studies, a larger amount of particles were generated in the material, which burned for a longer time. Particle levels measured in flue gas showed a wide distribution of particles with the overall mass distribution in the range of 0.1–0.3 μm [7].

To understand how the transport of fire-born particles (FBPs) with water from firefighting operations affects contaminant transport requires understanding of the types of particles in the extinguishing water and their interaction with pollutants. Particle properties will affect their transport properties as well as the impact of particle interaction with the pollutants. Polycyclic aromatic hydrocarbons (PAHs) and metals are two groups of substances of environmental concern, which are commonly found in runoff water from fires at concentrations exceeding drinking water standards [1,9,10]. However, the characteristics of these particles when present in the extinguishing water, including properties affecting transport and interaction with other particles and contaminants are to date not well documented.

It is also critical to understand how the chemical signature of the water carrying the particles affects the transport. During fire-extinguishing operations the water chemistry can be strongly affected by the fire and the specific materials that are present and burning on the site. Upon infiltration into the ground, in contact with soil and mixing with soil and groundwater, this signature may start to change, affecting the transportability of FBPs. Water chemistry parameters such as pH and salt concentration are well known to affect particle transport in porous media (e.g., [11–16]). While water chemistry can vary strongly for different fires and extinguishing operations, it is important to understand how these parameters influence the particle mediated contaminant transport and ultimate fate of the fire-generated contamination.

A number of studies exist regarding fire-generated particles in air (e.g., [7,8]) but a thorough understanding of the properties of fire-born particles carried with the extinguishing water is still lacking. In order to understand and predict the subsurface transport and environmental impact of FBPs, it is necessary to understand their chemical and physical properties and their interaction with other constituents in the extinguishing water and soil system. The main objective of this study is to quantify the physical and chemical properties of the particles commonly found in discharge water from fire extinguishing operations and to predict the fate and transport of these particles in soil and groundwater. This case study is based on collection of original samples from several points related to the same fire in a warehouse facility in Uppsala, Sweden. A detailed characterization of the particles present in the extinguishing water was performed. Metal and PAH contaminants associated with the

particles were quantified, and the properties related to the transportability of the particles in subsurface systems were measured including particle-size distribution, particle surface charge, and structures of the particles. Further, a series of column transport experiments in a controlled environment were performed using one of the collected firefighting water samples for varying water chemistry and physical conditions.

2. Materials and Methods

2.1. Sampling of Fire-Extinguishing Water

During autumn 2013, a fire occurred in a store and warehouse in Uppsala, Sweden, for tiles and miscellaneous tools. The part of the building that was most exposed by the fire was a shop, where tools were kept in plastic containers as well as a staff room with kitchen and wooden furniture. Upon extinguishing the fire, the fire department used approximately 50 m³ of water, but no additives were used in the water. At the fire location, foam was observed in the runoff water in contact with the burned materials. The ground surface in and around the building consisted mainly of hardened surfaces, which resulted in pooled extinguishing water on these surfaces.

Water from the fire area was collected at three different points in the building near the most fire-prone locations. The sampling was done six days after the fire was extinguished. The collected water was deemed to be representative and relatively unchanged during this time period because it was pooled indoors under roof and on impermeable surfaces. Sampling site 1 was in the doorway to the room where the most intense fire occurred, sampling site 2 was on the floor outside this room and sampling site 3 was located in an area near site 2 where bags of cement powder were stored and the extinguishing water may have been affected by these materials. After collection, the samples were stored in glass and plastic bottles (depending on the planned analysis) until the analyses were carried out.

2.2. Characterization of Fire-Born Particles in the Extinguishing Water

The physical and chemical properties of the FBPs in sampled water were analyzed for each sampling site. All three original samples were used for measurement of pH and electrical conductivity (Table 1). The zeta potential of the FBPs was measured using a Zeta-Sizer (Malvern Instruments, Malvern, UK). Later, three sets of original fire extinguishing water samples from all three locations were prepared for the analysis of various metals and PAHs using Inductively Coupled Plasma/Mass spectroscopy (ICP/MS) and Gas Chromatography/Mass Spectroscopy (GC/MS) respectively at ALcontrol Laboratories, Linköping, Sweden. Samples from the second site were used for column transport experiments. This sample was filtered through an 11-µm membrane filter so that both particles smaller and greater than 11 µm could be analyzed for metals and PAH at ALcontrol Laboratories. The sample for filtered material of particles >11 µm was prepared by adding an equal amount of de-ionized (DI) water to the filtered material collected from the membrane filter. In addition to the chemical characterization of extinguishing water samples, two sets of samples (with particles <11 µm and <100 µm) were used for visualization and image analysis using Scanning Electron Microscopy (Leo 1550, Field Emission Scanning Electron Microscope, Jena, Germany).

Table 1. Characteristics of fire born particles (FBPs) in extinguishing water and column experiment parameters.

Experiment No.	FBP Size Range (μm)	Background pH (-)	Electrical Conductivity (mS/cm)	FBP Zeta Potential (mV)	Porous media		Flow Rate (mL/min)	Porosity (-)
					Size Range (μm)	Average		
Sample 1	<100	8.64	4.06	−10.1	N.A.	N.A.	N.A.	N.A.
Sample 3	<100	7.72	3.02	−10.7	N.A.	N.A.	N.A.	N.A.
Sample 2								
1	<11	9.8	3.83	−5.76	250–400	325	1	0.33
2	<100	9.8	3.83	−5.76	250–400	325	1	0.33
3	<11	9.8	3.83	−5.76	400–500	450	1	0.33
4	<11	9.8	3.83	−5.76	177–250	213	1	0.34
5	<11	9.8	3.83	−5.76	125–177	151	1	0.34
6	<11	6.5	3.83	−4.06	250–400	325	1	0.33
7	<11	3	3.83	−3.11	250–400	325	1	0.33

N.A.: Not applicable.

2.3. Porous Media

Quartz sands (Sibelco Nordic, Baskarp, Sweden) with four different grain size distributions were used in this study. The sand was sieved to fine (0.125–0.177 mm), medium 1 (0.177–0.225 mm), medium 2 (0.25–0.4 mm), and coarse (0.4–0.5 mm) grain sizes. To remove all the impurities, the sand was washed using the same procedure as Mekonen *et al.* [15]. In brief, it was sequentially cleaned by 0.1 M hydrochloric acid (37%–38%) solution for 30 min, and then flushed and rinsed several times by DI water. The sand was then washed by 30% H₂O₂ and DI water with a volumetric ratio of 8:35 in the shaking flask for a total 40 min by stirring the sand every 10 min. Finally, the sand was washed by DI water and placed in the oven at 105 °C for 24 h. The rinsed and dried sand was labeled and stored in a clean plastic bottle.

2.4. Experimental Setup

Transport experiments were performed using a cylindrical glass column with 15 cm length and 2.5 cm diameter. A steel mesh filter (0.2 mm) was used on both sides of the glass column in order to stop the sand from entering into the tubing. The tubes connected to the column were flushed and filled with background solution to remove air bubbles before starting the experiment. A three-way valve was used to control the type of liquid flow (extinguishing water samples or background solution). The column was wet-packed in order to avoid any trapped air in the column. A high precision peristaltic pump (IPC8, Ismatec, Wertheim, Germany) was calibrated and used for injection of the samples at the chosen flow rates. The column effluents were collected by a fraction collector (CF-2, Spectrum Labs Inc., Breda, The Netherlands) and the concentration was measured by UV/VIS spectrophotometer (DR 5000, Hach Lange Ltd., Salford, UK) at a wavelength of 334 nm after a complete wavelength scanning. In addition, a number of tracer tests (using Brilliant Blue R, Sigma Aldrich, Stockholm, Sweden) were conducted separately to obtain the breakthrough curves with different collector grain sizes at the selected flow rates. The injected tracer concentration was 20 mg/L and the breakthrough concentrations were quantified at 300 nm wavelength using the spectrophotometer.

2.5. Column Experiments

Column experiments were performed to examine transport of the FBPs through a porous medium using sample number 2 only for different experimental condition listed in Table 1. First, the column was flushed with the corresponding aqueous solution at high flow rate for 10 pore volumes. Then, the flow rate was reduced to the experimental flow rate of 1 mL/min for another 2 pore volumes. Once the absorbance of the effluent sample had reached the background level (absorbance less than detection limit of the spectrophotometer), the experiment was performed. The water sample was first injected

for 5.2 pore volumes (phase 1), and then the sand column was flushed with background solution for another 5.2 pore volumes (phase 2). Finally, DI water was injected for another 3 pore volumes (phase 3) in order to lower the ionic strength and study remobilization of particles related to deposition at secondary energy minima. Each column experiment was repeated twice for the experimental conditions shown in Table 1. Two sets of column experiments were conducted using water samples collected from site 2 after filtering them using 11 µm and 100 µm filter membranes, respectively. Three sets of column experiments were performed after adjusting the pH of water samples (filtered to particle sizes less than 11 µm) and background samples. Four sets of column experiments were also conducted at the original pH of the collected samples but changing the porous media grain sizes. The electrical conductivity of the samples was measured using a conductivity meter and the equivalent conductivity of the background solution during phase 2 was adjusted using NaCl salt solution.

3. Results and Discussion

3.1. Characterization of Fire-Born Particles

The concentrations of the 16 measured polyaromatic hydrocarbons from the three different sampling locations are shown in logarithmic scale in Figure 1. The figure indicates the highest concentration of all form of PAH in sample 1 and lowest in sample 3. The compounds from benzo[a]anthracene and to the right in Figure 1 are considered to be of high molecular weight [17] and these, except benzo[ghi]perylene, are also considered carcinogenic (e.g., [18–22]). Low molecular weight PAHs may be found in the gas phase whereas the high molecular weight PAHs, which are also of greater environmental concern, have very low volatility and will generally be found in particles. All measured PAHs were found at all three sampling locations, and the relative abundance of the compounds was in relative agreement with previous studies (e.g., [23]) although, comparatively, somewhat lower concentrations of the low molecular weight PAHs were observed. This may be due to some volatilization of low molecular weight PAHs before sampling was performed. The differences in concentrations between the different sampling locations was likely related to the fact that the extinguishing water was found in different state of concentration at the different locations, and, particularly, large amounts of black soot was observed at location 1. However, the local thermo-physical characteristics of the fire and the burning materials should also have influenced the proportion of different compounds that were locally formed. The sum of carcinogenic PAHs was larger than 10 times the Swedish guideline value for groundwater at all sampling locations ($>10 \times 0.2 = 2 \mu\text{g/L}$), which (undiluted) would be considered a “very serious” state of contamination [24].

The concentrations of the 10 measured metals at the three different sampling locations are shown in logarithmic scale in Figure 2. The relative difference in metal concentrations between the different sampling locations is small as compared to the PAHs (Figure 1), which may indicate less influence of local factors on the amount of metal particles formed in the fire. Some of the metals (Cd, Cu, Zn, etc.) were highest in sample 1, but they don't follow any proper order. The metal concentrations are also in relative agreement with previous findings [23]. The concentrations of Pb, Cd, Cu and Zn were more than 10 times the Swedish water quality guideline values [24] for all samples. For As, Cr and Ni, the concentrations were above the guideline values, whereas for Ba, Co and V, Swedish guideline values have not been established.

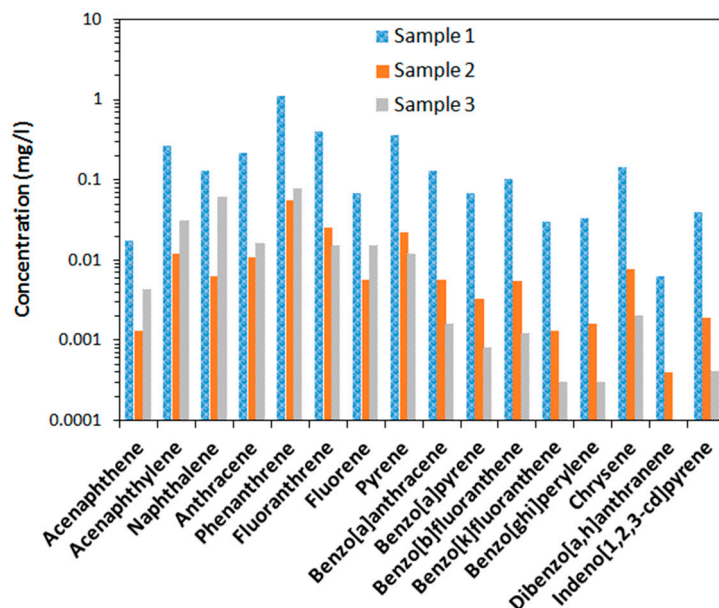


Figure 1. Concentration of PAHs in the collected fire extinguishing water samples from three different locations.

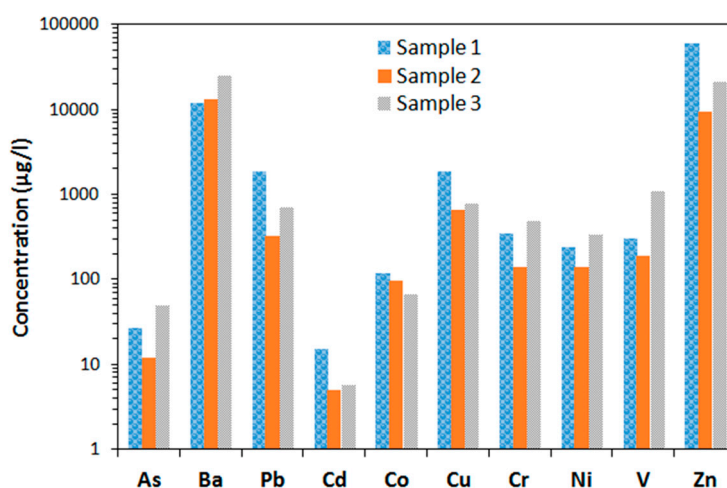


Figure 2. Concentration of metals in the collected fire extinguishing water samples from three different locations.

A critical factor for the mobility of particles in porous media is the size of the particles. It is therefore interesting to investigate how contaminants are distributed between different sizes of particles. This has also not previously been done for fire-generated particles in the extinguishing water. As shown in Figure 3, the concentrations of PAHs were typically at least one order of magnitude lower in the particle solution filtered to sizes $<11\ \mu\text{m}$ compared to the solution of sizes greater than $11\ \mu\text{m}$ and less than $100\ \mu\text{m}$. The difference was more pronounced for the high molecular weight (and carcinogenic) PAHs, which indicates that these may have a larger tendency to form larger particles or aggregates as compared to the lower molecular weight PAHs. The summed concentration of carcinogenic PAHs was, however, still slightly larger than the Swedish groundwater quality guideline value of $0.2\ \mu\text{g/L}$ even for the particles of size $<11\ \mu\text{m}$. Concentrations in the unfiltered sample were higher than in the $<100\ \mu\text{m}$ filtrate, indicating that particles or aggregates $>100\ \mu\text{m}$ existed in the original sample.

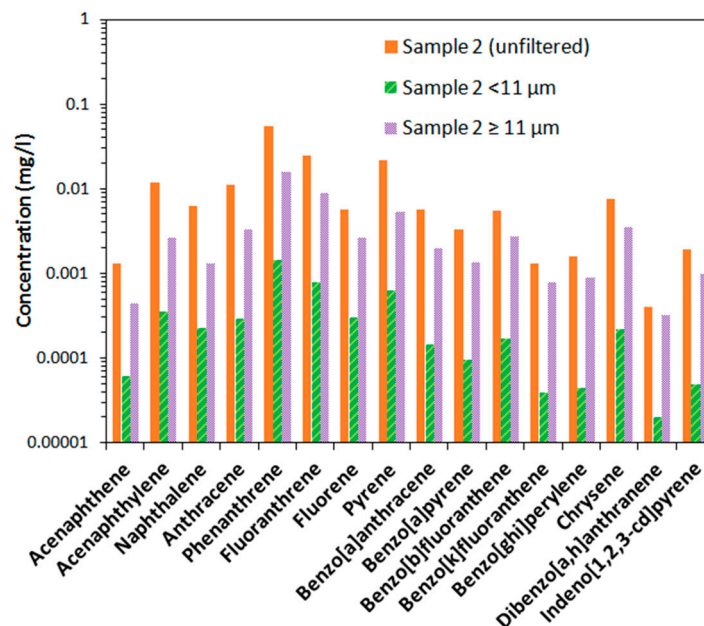


Figure 3. Concentration of PAHs in filtered and unfiltered samples at location 2.

As shown in Figure 4, six of the measured metals; As, Ba, Pb, Cd, Cr and Zn, had concentrations of at least one order of magnitude lower in the <11 μm filtrate compared to in particles between 11 μm and 100 μm. This indicates that these metals tend to be associated with larger particles, which may also be related to affinity of these metals to attach to larger soot particles. Four metals—Co, Cu, Ni and V—did not appear in significantly higher concentrations in the filtrate with larger particles. Co and Ni were even found in higher concentrations in the filtrate of smaller size particles (<11 μm). There appear to be a difference in characteristics between different metals, and the latter four may be less prone to aggregate. Contaminants found in smaller particles may also have larger mobility with water flowing through porous media, as will be further investigated in the following sections.

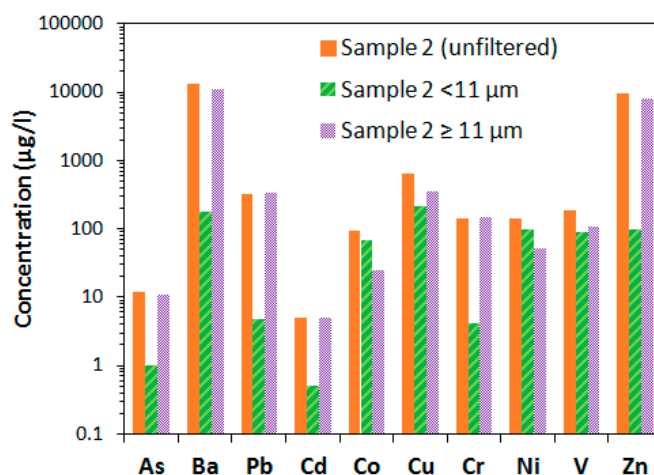


Figure 4. Concentration of metals in filtered and unfiltered samples at location 2.

3.2. Physical Factors for Transport of Fire-Born Particles in Porous Media

A set of column experiments with FBPs filtered to sizes <100 μm and <11 μm was conducted. As can be seen in Figure 5, the outflow concentrations from the column for samples filtered to less than 11 μm were close to their original (inflow) concentration. However, the outflow concentrations from

the column for samples filtered to sizes less than 100 μm (note that this sample also contains particles $<11\ \mu\text{m}$ as opposed to in the chemical analyses) were much less than their original concentration. The steady state relative concentration of FBPs for finer sizes ($<11\ \mu\text{m}$) was approximately 1, which means that the retention of these particles was negligible. It further indicates that attachment of FBPs did not occur at the natural chemical condition of the extinguishing water in combination with the selected physical condition (flow rate and porous media). However the results for FBPs $<100\ \mu\text{m}$ showed partial retention; at the same physical and chemical conditions, only 33% of the total particle concentration flowed through the column. The 77% retained particles in the column could not be mobilized even after changing the background solution to DI water (phase 3). It suggests that the particle larger than 11 μm were not deposited at the secondary energy minima locations. However, the result indicates that the selected porous media filtered out the larger particles in between 11 and 100 μm . Physical screening/straining was the likely retention mechanism in this scenario for FBPs, and other retention mechanisms should not have played any major role, as the remobilization of FBPs was negligible in phase 3 of the column experiment. Figure 6 shows the SEM images of FBPs for inflow and outflow samples from the column for both size ranges ($<11\ \mu\text{m}$ and $<100\ \mu\text{m}$). The particles $<11\ \mu\text{m}$ were nearly spherical in shape and show a similar distribution in images of inflow and outflow solution (Figure 6a,b). This is in agreement with the column experiment results for this size range. However, the image of the inflow solution for particles $<100\ \mu\text{m}$ (Figure 6c) was quite different (fibrous structure) from that of the outflow solution (Figure 6d), where spherical shaped particles similar to the those in the sample filtered to sizes $<11\ \mu\text{m}$ can be observed. Thus, the larger fibrous kind of particles was filtered out during the flow through the porous media in the column. It can also be concluded that the FBPs $<11\ \mu\text{m}$ were highly mobile under the conditions tested here, posing a risk to reach the groundwater if they infiltrated into a subsurface system.

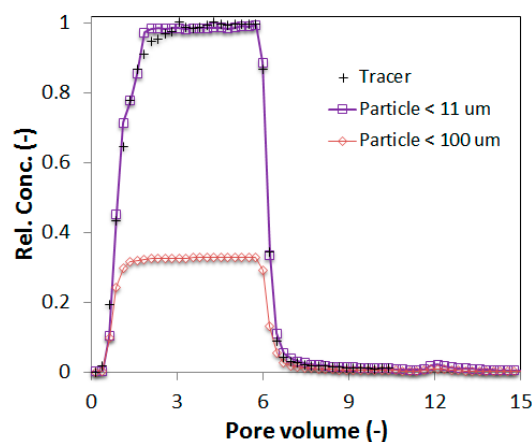


Figure 5. Representative FBP breakthrough curves from column experiments using extinguishing water collected at site 2 after filtration using two different particle sizes.

Column experiments for FBP transport through a wide range of porous media particle size distributions were conducted while keeping other physical and chemical conditions constant. Figure 7 shows the column outflow breakthrough curves for four porous media sizes with average sizes of 450 μm , 325 μm , 213 μm , and 151 μm , respectively. The results indicate that the FBPs are completely mobile in the three largest porous media grain sizes, while in the smallest grain size a small portion of approximately 2%–3% of the FBPs were retained. A small peak of remobilization could be observed in phase 3 in these experiments (Figure 7) but was not significant in terms of the total inflow mass of FBPs to the column. It can be concluded that even the average grain size of 151 μm (range 125–177 μm) was big enough to allow nearly full mobility of FBPs of sizes up to 11 μm . It can be noted that these FBPs were still more than one order of magnitude smaller than the sand grain size.

This further confirms that the retention mechanism for larger FBPs is likely be straining, and no other retention mechanisms were operative for the present experimental scenarios.

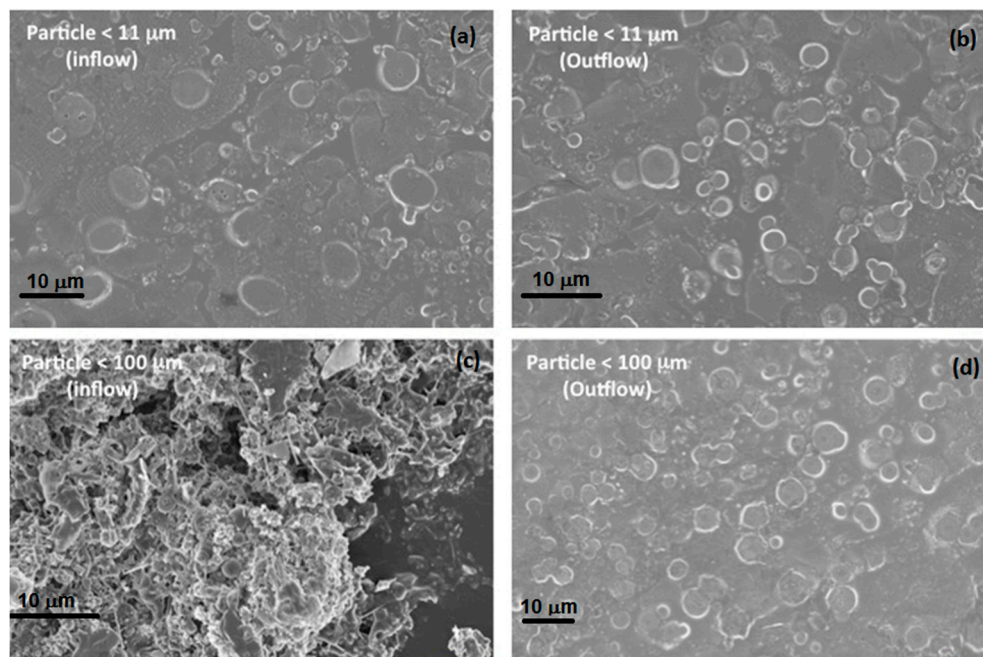


Figure 6. Scanning electron microscope images for fire-born particles from sampling site 2 for: (a) column inflow particle solution <11 μm ; (b) column outflow particle solution <11 μm ; (c) column inflow particle solution <100 μm ; (d) column outflow particle solution <100 μm .

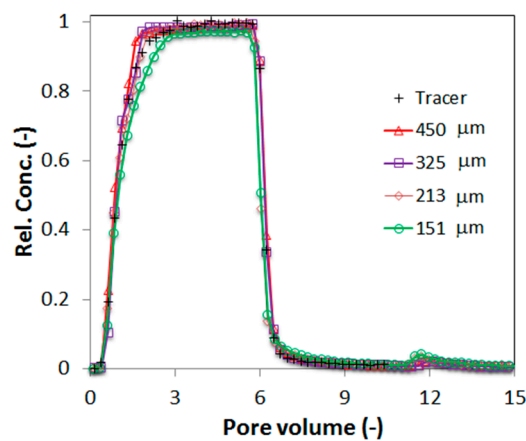


Figure 7. Representative FBP breakthrough curves from column experiments using fire extinguishing water collected at site 2 with four different porous media grain sizes.

3.3. Background Chemistry for Transport of Fire-Born Particles in Porous Media

The effect of background solution chemistry was also tested in this study. The ionic strength was not possible to vary in these fire extinguishing water samples because the salt concentration was very high (approximately 60 mM). The original pH of the fire extinguishing water was also high so the variation of solution chemistry is based on lowering the pH, as shown in Table 1. The effects of pH change on FBP outflow concentrations are shown in Figure 8. The results indicate that the relative concentration decreases with a decrease in solution pH. The relative concentration was close to 1.0, 0.92, and 0.88 for pH equal to 9.8, 6.5, and 3.0 respectively. An increase in retention of

colloids/nanoparticles with a decrease in pH has been observed in several previous studies (such as, [15,16,25]). The Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction forces between FBP and sand surfaces might change due to a decrease in pH. The measurements presented in Table 1 show an increase in surface charges with a decrease in solution pH, which can favor particle retention at secondary energy minima. The surface charges are also in agreement with the absence of a secondary peak during phase 3 for pH 9.8 while small peaks were present for pH 6.5 and 3.0 (Figure 8). These results indicate a partial retention of FBPs at very low pH, however, at pH representative of natural soil and groundwater (pH 6.5), the FBPs had nearly full mobility.

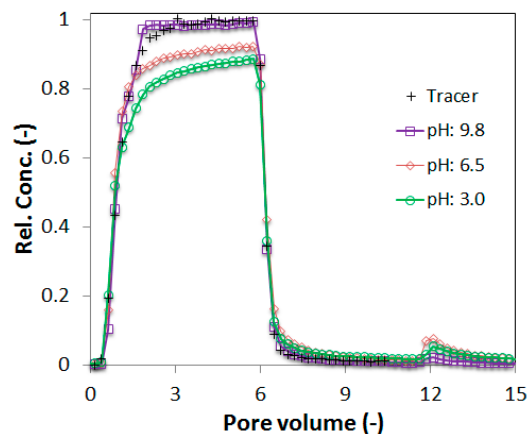


Figure 8. Representative FBP breakthrough curves from column experiments using fire-extinguishing water collected at site 2 adjusted to three different pH.

3.4. Mass Balance and Total Retention of Fire-Born Particles

An integration of total particle mass was done to calculate the ratio of outflow mass to inflow mass. Figure 9 shows the mass ratios for the different physical and chemical condition tested in this study. A high mass ratio indicates low retention of particles. The mass ratio was much higher for small size ($<11\ \mu\text{m}$) FBPs than the larger ($<100\ \mu\text{m}$) particles (Figure 9a). It can also be noted that the actual outflow mass was in the same order for both cases (data not shown here), which indicates that most of the filtered/strained FBPs were in the range of 11 to $100\ \mu\text{m}$.

The mass ratio for phases 1 and 2 are plotted in Figure 9b as a function of average grain size. Although the absolute differences in retention were relatively small, a clear trend of increase in outflow mass with increase in grain size could be observed (Figure 9b). Physical straining was the likely retention mechanism.

Figure 9c shows the effect of pH on the outflow to inflow mass ratio. There is a clear trend of increase in outflow mass of FBPs with increase in pH. As discussed in the previous section, deposition at secondary energy minima is a possible retention mechanism at low pH, which was also supported by the observed remobilization of FBPs in phase 3.

From this study, we attempted to identify the presence of harmful contaminants (metals and PAH) in different sizes of fire burned particles from the selected location then we tried to represent the extreme pH condition for possible mobilization of these contaminant attached fire particles in porous media in order to warn the agencies involved in fire fighting operations (to save the ground- or surface-water pollution).

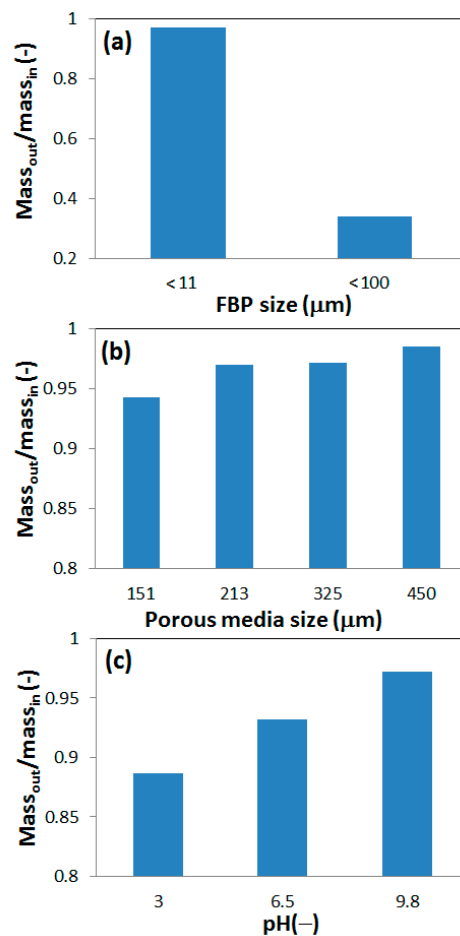


Figure 9. Ratio of outflow to inflow mass of FBPs in column experiments for: (a) FBPs filtered to sizes <11 μm and <100 μm , respectively; (b) different porous media grain sizes; (c) different pH of solution.

4. Conclusions

Detailed characterization of fire extinguishing water is important to understand both the contamination content and the potential subsurface mobility of the contaminants present. This can be fire and site specific. Depending on the type of fire, a number of contaminants such as metals and polycyclic aromatic hydrocarbons can be present in the fire-generated particles. The transport and retention of fire-born particles (FBPs) upon infiltration to soil and groundwater systems are, however, also influenced by the physical and chemical conditions of the soil and the water carrying the particles. Some of the key characteristics that affect transport of fire-born particles in water-saturated soil and groundwater are their surface charge, size, and the solution chemistry of the water that carries them. Size affects physical straining while surface charge and solution chemistry influence the physicochemical mechanisms of particle and surface interactions. Sand grain size had only a small influence on the transport of smaller particles (<11 μm) through the column. For these particles, retention was only observed when the water chemistry was changed. The magnitudes of the negatively charged particle surface were less at low pH, which resulted less retention (*i.e.*, some particles being attracted to the sand grains leading to deposition at energy minima). The larger particles (>11 μm and <100 μm) had almost no mobility in the porous media, which might have filtered out by physical straining mechanism. The chemical analyses showed that the main part of the PAH content consists high molecular weight carcinogenic PAHs, which were found in the larger particles (>11 μm), while the total PAH content were predominant in the smaller particles (<11 μm). For metals, a similar behaviour was observed for As, Ba, Pb, Cd, Cr and Zn, while Co, Cu, Ni and V were almost equal for both finer

(<11 µm) and larger (>11 µm) particles. In combination with the results for particle mobility, this study also indicates that a large portion of the PAHs and several metals of high environmental concern were likely be filtered out to a large extent in the top soil upon infiltration to the ground. However, those contaminants associated with small particles (<11 µm) are likely to be highly mobile with the infiltrating water and may pose a threat of groundwater contamination. Although the main part of the total contaminant load was found in larger, immobile particles, the current results indicate that both PAHs and metals may be found at concentrations exceeding groundwater quality guideline values in the fraction of smaller mobile particles. Future research would be beneficial to further investigate a broader range of fires and local soil conditions.

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Author Contributions: Prabhakar Sharma has designed the main experimental work, monitored the implementation of the work in the laboratory, and prepared the manuscript. Fritjof Fagerlund planned and initiated this work after discussions with the Swedish Civil Contingencies Agency and also took part in the design of the experiments. Ulrika Iverfeldt and Amanda Eskebaek performed the sample preparation and conducted the flow through column experiments in the laboratory. The data analysis part was performed through discussion among all authors.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Myndigheten för Samhällsskydd Och Beredskap (MSB). *Bränder*; Myndigheten för Samhällsskydd Och Beredskap: Stockholm, Sweden, 2012.
2. Särdaqvist, S. *Vatten Och Andra Släckmedel*; Räddningsverket: Karlstad, Sweden, 2006.
3. Norberg, P.; Lithner, D. *Rening Och Destruktion av Kontaminerat Släckvatten*; Myndigheten för Samhällsskydd Och Beredskap (MSB): Stockholm, Sweden, 2013.
4. Hertzberg, T. *Partiklar Från Bränder—Förstudie*; Sveriges Provnings och Forskningsinstitut (SP): Borås, Sweden, 2001.
5. Butler, K.M.; Mulholland, G.W. Generation and transport of smoke components. *Fire Technol.* **2004**, *40*, 149–176. [CrossRef]
6. Noiton, D.; Fowles, J.; Davies, H. *The Ecotoxicology of Fire-Water Runoff Part II—Analytical Results*; New Zealand Fire Service Commission: Wellington, New Zealand, 2001.
7. Hertzberg, T.; Blomqvist, P. Particles from fire—A screening of common materials found in buildings. *Fire Mater.* **2013**, *27*, 295–314. [CrossRef]
8. Blomqvist, P.; Simonson, M.; Stec, A.A.; Gylestam, D.; Karlsson, D. *Characterisation of Fire Generated Particles*; BRANDFORSK Project 700-0601 (SP Rapport 2010:01); Sveriges Provnings och Forskningsinstitut (SP): Borås, Sweden, 2010.
9. Leifeld, J.; Fenner, S.; Muller, M. Mobility of black carbon in drained peatland soil. *Biogeosciences* **2007**, *4*, 425–432. [CrossRef]
10. Diblasi, C.J.; Li, H.; Davis, A.P.; Ghosh, U. Removal and fate of polycyclic aromatic hydrocarbon pollutants an urban stormwater bioretention facility. *Environ. Sci. Technol.* **2009**, *43*, 494–502. [CrossRef] [PubMed]
11. Elimelech, M.J.; Gregory, X.J.; Williams, R.A.; Gregory, J.; Xiaodong, J.; Williams, R.A. *Particle Deposition & Aggregation—Measurement, Modelling and Simulation*; Elsevier: Philadelphia, PA, USA, 1995.
12. Sharma, P.; Abdou, H.M.; Flury, M. Effect of the lower boundary condition and flotation on colloid mobilization in unsaturated sandy sediments. *Vadose Zone J.* **2008**, *7*, 930–940. [CrossRef]
13. Sharma, P.; Flury, M.; Zhou, J. Detachment of colloids from a solid surface by a moving air-water interface. *J. Colloid Interface Sci.* **2008**, *326*, 143–150. [CrossRef] [PubMed]
14. Sharma, P.; Flury, M.; Mattson, E.D. Studying colloid transport in porous media using a geocentrifuge. *Water Resour. Res.* **2008**, *44*. [CrossRef]
15. Mekonen, A.; Sharma, P.; Fagerlund, F. Transport and mobilization of multiwall carbon nanotubes in quartz sand under varying saturation. *Environ. Earth Sci.* **2014**, *71*, 3751–3760. [CrossRef]

16. Sharma, P.; Bao, D.; Fagerlund, F. Deposition and mobilization of functionalized multiwall carbon nanotubes in saturated porous media: Effect of grain size, flow velocity and solution chemistry. *Environ. Earth Sci.* **2014**, *72*, 3025–3035. [CrossRef]
17. Sterner, O. *Förgiftningar Och Miljöhot*; Studentlitteratur: Lund, Sweden, 2003.
18. Nisbet, I.C.; LaGoy, P.K. Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). *Regulatory Toxicol. Pharmacol.* **1992**, *16*, 290–300. [CrossRef]
19. Ruokojärvi, P.; Aatamila, M.; Ruuskanen, J. Toxic chlorinated and polyaromatic hydrocarbons in simulated house fires. *Chemosphere* **2000**, *41*, 825–828. [CrossRef]
20. Larsson, I.; Lönnermark, A. *Utsläpp Från Bränder—Analyser av Brandgaser Och Släckvatten*; BRANDFORSK Projekt 707-021 (SP Rapport 2002:24); Sveriges Provnings och Forskningsinstitut (SP): Borås, Sweden, 2002.
21. Lönnermark, A.; Blomqvist, P. *Emissions from Fires in Electrical and Electronics Waste*; Sveriges Provnings Och Forskningsinstitut (SP): Borås, Sweden, 2005.
22. Lönnermark, A.; Blomqvist, P. *Emissions from Tyre Fires*; Sveriges Provnings Och Forskningsinstitut (SP): Borås, Sweden, 2005.
23. Blomqvist, P.; Lönnermark, A.; Simonson, M. *Miljöbelastning vid Bränder Och Andra Olyckor—Utvärdering av Provtagning Och Analyser*; Räddningsverket: Karlstad, Sweden, 2004.
24. Naturvårdsverket. *Metodik för Inventering av Förorenade Områden—Bedömningsgrunder för Miljökvalitet—Vägledning, Rapport 4918 för Insamling av Underlagsdata*; Naturvårdsverket: Värnamo, Sweden, 1999.
25. Sharma, P.; Fagerlund, F. Transport of surface-modified carbon nanotubes through soil and groundwater. *J. Vis. Exp.* **2015**. [CrossRef] [PubMed]



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