The Open Civil Engineering Journal, **2011**, *5*, **17-24**

Do Deicing Agents Affect the Quality and Quantity of Aliphatic and Polyaromatic Hydrocarbons in Asphalt Pavements?

K.M. Kalevi and J.M. Salminen*

Centre for Comsumption and Production, Finnish Environment Institute, P.O. Box 140, FI-00251 Helsinki, Finland

Abstract: Chemical deicing plays a fundamental role for traffic safety on roads and runways in winter season. Traditional deicing chemicals, such as sodium chloride and urea have, however, undesirable effects on surface and ground waters. For more sustainable road and runway winter maintenance, easily biodegradable organic salts such as acetates and formates, have been proposed and taken into use. Next to environmental impacts, deicing chemicals may also affect asphalt pavements. This paper investigates whether traditional or alternative deicers change the quality or quantity of polyaromatic and aliphatic petroleum hydrocarbons in asphalt pavements. Asphalt core samples were taken from two highways and two airports in Finland and analyzed for polyaromatic and aliphatic petroleum hydrocarbons, residual deicer chemicals, and hydraulic conductivities. Results for similar pavements exposed to different deicers were compared. In addition, heat treatment experiments were conducted for the core samples. The current study shows that deicers change neither the quality nor the quantity of polyaromatic and aliphatic petroleum hydrocarbons. No changes were recorded in samples heated up to 100 °C.

Keywords: Deicing, Asphalt pavements, Bitumen, Airport runways, Highway and road management.

INTRODUCTION

Chemical anti-icing and deicing play an essential role in the winter maintenance of roads and airports in the northern hemisphere. The principal requirement for a deicing chemical is that it has to have a melting capacity over a range of temperatures. On the other hand, chemicals corrosive to aircrafts may not be used on runways or taxiways. Consequently, chloride salts are not applied at airports while they are commonly used for road deicing. In the recent years, environmental consequences of anti-icing and deicing have gained more attention in road and airport winter maintenance [1, 2]. Urea is known to cause eutrophication and oxygen depletion in water environments [1]. Sodium chloride originating from deicing impairs groundwater quality and poses risks to present or future drinking water production [1]. Disadvantages attributed to the traditional deicers, urea and chloride salts, have given space to alternative products such as formate- and acetate-based salts, which are used at airports since the beginning of the 1990s [3]. Their suitability for road deicing has also gained interest [1, 4, 5].

Shi *et al.* [3] pointed out that deicer chemicals' effectiveness, environmental impacts and corrosion risks are among the most relevant criteria considered by airports for the choice of a deicing product. However, deicers may also have impacts on (asphalt) pavements (for review, see Shi *et al.* [6]). Previously, Hassan *et al.* [7] investigated the effects of freeze-thaw cycles and various deicers on concrete asphalt pavements. They reported that the presence of deicer-containing water solutions had a damaging effect on asphalt mixes and their physical properties in comparison with parallel samples kept dry. However, only urea seemed to have higher deleterious impacts on the mechanical properties of asphalt concrete while the rest of the chemicals tested (sodium chloride, potassium acetate, and sodium formate) had effects comparable to that of distilled water. Maximum damaging effects were recorded at a deicer concentration range from 1 to 2 %. According to the authors, freeze-thaw cycles softened and deicing chemicals hardened the pavement samples. More recently, Alatyppö *et al.* [8] raised concerns that formate and acetate salts may seriously damage asphalt pavements. They suggested that introduction of formate and acetate into the asphalt pavements results in changes in the quality and quantity of aliphatic petroleum hydrocarbons (PHCs) and polyaromatic hydrocarbons (PAHs) through a chemical reaction between bitumen and formate/acetate. According to Alatyppö *et al.* [8], these changes were related to considerable damages and subsequent performance failure of pavements at two Finnish airports where formate/acetate salts had been used. The researchers also indicated that an increase in the concentrations of aliphatic PHCs and PAHs, and signs of pavement durability problems could be found in highway pavements samples on a stretch where potassium formate had been used as a sole deicer since 2002 [8]. Alatyppö *et al.* [8] suggested a mechanism, where heat, moisture,

---

*Address correspondence to this author at the Centre for Comsumption and Production, Finnish Environment Institute, P.O. Box 140, FI-00251 Helsinki, Finland; Tel: +358 400 14861; Fax: +358 9 5490 2391;
E-mail: jani.salminen@ymparisto.fi

and acetate or formate are required for the damage process to occur. This mechanism, however, was not fully investigated nor proven [8] and the issue thus remained controversial.

The present work aimed at finding out whether there were changes in the concentrations of aliphatic PHCs and PAHs in the asphalt pavements at Finnish airports and highways where formate and/or acetate salts are applied. Moreover, experiments were carried out to reveal whether these changes could be created in a laboratory by heating potassium formate containing asphalt pavement samples. To assess deicer penetration into the pavements, the residual deicer concentrations in pavement cores shortly after the deicing season, and the cores' water permeability values were determined.

MATERIALS AND METHODS

Sampling and Study Sites

Asphalt pavements on two airports and two stretches of highways were sampled. Details on sampling locations, number of replicate samples, and characteristics of the asphalt pavements sampled are listed in Table **1**.

On Hwy 13, potassium formate has been used as a sole deicer since 2002 on a stretch of 1.7 km [2]. Prior to 2002, sodium chloride was used for deicing for approximately 20 years. On Hwy 6, potassium formate has been used since 2005 on a stretch of 5 km. Core samples were also taken from the airports of Helsinki and Kuopio. At Helsinki airport, acetate is applied since 1989, formate since 1998, and since 1996 only acetates and formates (and no urea) are used [9]. At Kuopio airport, acetate was introduced in 1993, formate 2002, and since 2001 urea is no longer applied [9]. The average loads of deicers applied in 2002-2007 at these 4 sites are presented in Table **1**.

The pavement cores taken contained all the layers laid in the past at the sampling site, and the analyses were performed from separate layers for most of the samples. The sampling locations were chosen as follows: At highways, samples were taken from stretches where sodium chloride is applied and from stretches where potassium chloride is applied since 3-5 years. Moreover, the corresponding pavements from NaCl- and KFo-receiving stretches at Hwy 13 or Hwy 6 were of the same origin, manufacturer, date, and batch to assure that the core samples within an individual site were fully comparable. At airports, core samples were taken from areas receiving high loads of organic deicers (acetate and formate salts) and from reference areas with low exposure to these chemicals. Kuopio airport, however, does not have sites that do not receive any deicers. For that sake sampling was done at the end of the runway, where deicer load was anticipated to be lower than elsewhere at the airfield. In addition, a sample from fresh asphalt mix was taken upon the repaving at Kuopio airport in summer 2007 to allow comparisons between samples exposed to deicers and a sample completely unexposed to deicers of any kind.

Analyses of PAHs and Aliphatic PHCs

The concentrations of 16 PAHs and aliphatic PHCs in the maltene fraction of the bitumen in the pavement samples were determined by using a method modified from Kolak and Burruss [10] and Yan *et al.* [11]. First, 14±4 g of crushed and homogenized pavement sample was extracted with 15 ml of *n*-hexane (pa quality, Merck) in screw-capped glass bottles by shaking the sample for 18 h at 100 rpm. The *n*-hexane was then transferred into a separate vial. Additional 5 ml of *n*-hexane was then added into the bottle, which was then mildly shaken. The solids were allowed to precipitate and the supernatant was transferred to the vial. Residual *n*-hexane was allowed to evaporate for 24 h at room temperature where after the residual mass of the sample was weighted to calculate the mass of the malthene fraction extracted. An aliquot of 1 ml was withdrawn from the 20-ml extract and indeno(1,2,3-cd)fluoranthene, *n*-decane (C_{10}), and *n*-hexadecane (C_{16}) were added as internal standards. The extract was then divided into two fractions in a column packed with 2.5 g of alumina (containing 5 % m/m water), 5 g of silica, and topped with a 1-cm layer of $NaSO_4$. Prior to the introduction of the extract, the columns were conditioned with 25 ml of dichloromethane and 25 ml of *n*-hexane. Aliphatic PHCs were first eluted with *n*-hexane and PAHs thereafter with *n*-hexane-dichloromethene (2:1). The range of aliphatic hydrocarbons detected with the method was determined as follows: individual compounds (C_{10}, C_{16}, *n*-tetracontane C_{40}, and *n*-pentacontane C_{50}) were dissolved in hexane and run in a gas chromatograph to determine their retention times and yields in the analysis. Based on the results obtained, aliphatic PHCs included in the analysis were estimated to range from C_{10} approximately up to C_{60}.

Table 1. Location of the Study Sites, and Details on Deicer Application, Pavement Layers and Replicate Samples

Site	Coordinates	Deicer(s) Applied	Deicer Load ($kg\ m^{-2}\ a^{-1}$)	No. of Asphalt Layers	No. of Replicate Core Samples
Hwy 13 at Suomenniemi	(68° 6'; 35° 22')	KFo	0.99	3	5
	(68° 8'; 35° 21')	NaCl	0.89	3	5
Hwy 6 at Taavetti	(67° 57'; 35° 30')	KFo	0.48	3	2
	(67° 57'; 35° 29')	NaCl	1.3	3	2
Helsinki airport	(66° 92'; 33° 87')	Acetates, formates	3.0	2	5+2[1]
Kuopio airport	(69° 89'; 35° 41')	Acetates, formates	0.33	3	5+2[1]

[1] number of samples from the taxiway/runway + number of reference samples.

As PHCs lighter than C_{16} were generally not found in the samples, they were excluded in the analysis.

Aliphatic PHCs in the range C_{16}-C_{60} were quantified by gas chromatograph (HP 6890N) equipped with flame ionization detector and a HP5 column (5 m, 320 µm, 0.25 µm). For this purpose, the total peak area from C_{16} onwards was measured. The peak area of C_{16} was integrated separately to obtain the recovery of C_{16} added into the sample upon the extraction. Concentrations of the 16 PAHs were determined by using gas chromatograph-mass spectrometer (Varian 8400/1200) equipped with VF-5ms column (25-30 m, 0.25 mm, 0.25 µm). The recovery of indeno(1,2,3-cd)fluoranthene was determined separately to assure the quality of the determination.

Analyses of Acetate, Formate, and Chloride

Roughly 150-300 g of crushed pavement core sample was put into a beaker glass and 150-200 ml of deionized water was added. Samples were let to stand (with occasional stirring) for 24 h where after the supernatant was separated and analyzed for formate and acetate by HPLC (Waters 501) equipped with an anion exclusion column and a diode array detector, and for chloride by using ion chromatograph (Dionex 500 with IonPac AS12A column).

Heating Experiments

Pavement core samples were first allowed to become saturated with either artificial rain water, with water solution containing 2.5-% of NaCl, or with water solution containing 5-% KFo. Saturated cores were then sawed into 4 pieces in vertical direction. One subsample was kept at room temperature, one was put into an oven at 55 ^{o}C for 15 min and another to 100 ^{o}C for 15 min. Then, the samples were allowed to cool down to room temperature. The heat treatment was followed by analyses of PAHs and aliphatic PHCs in the samples (including the subsamples which were not heated up).

Hydraulic Conductivity

Hydraulic conductivities of the pavement cores were determined in conductivity cells (Tampere University of Technology, Tampere, Finland) as follows. Core samples with thickness of 15 cm and a diameter of 10 cm were placed upside down onto a porous stone. Cores were carefully sealed with a rubber membrane and saturated either with synthetic rain water, or water containing 2.5 – 5 % potassium formate or sodium chloride. The solutions were introduced through the porous stone at a hydraulic gradient of 50-60. Once saturation of the samples had been reached, the flow through the core samples at a hydraulic gradient of 50-60 was monitored as a function of time yielding a value for hydraulic conductivity for the samples and solutions investigated.

RESULTS AND DISCUSSION

Aliphatic PHCs, and PAHs in Asphalt Pavements

In this study, concentrations of aliphatic PHCs, and 16 PAHs were analyzed in asphalt core samples from 2 airports and 2 highways that had received traditional and/or alternative deicing agents for years. Additionally, fresh asphalt mix was sampled and subjected to analyses of aliphatic PHCs and PAHs. This allowed a comparison between the concentrations in fresh, unexposed asphalt pavement with those having been exposed to deicers for years. In the following chapters, all PHC concentrations are reported per kg of bitumen's malthene fraction.

At Highways 13 and 6, no statistical difference in PAH-concentrations between NaCl- and KFo-receiving samples was recorded (Tables **2**, **3**). At Helsinki airport, the concentrations of PAHs were comparable to those found at Hwy 13 and Hwy 6 (Table **2**). At Kuopio airport, significantly higher concentrations (accompanied with high standard deviations) of PAHs were detected (Table **2**). After a repeated, layer-specific analysis of the Kuopio cores, high concentrations were found exclusively in the bottom layer: Concentrations up to 7770 mg/kg of PAHs were measured there (Table **2**). The bottom layer had been laid in the 1960's and contained tar [9]. At Kuopio airport, also the upper layers contained somewhat higher PAH concentrations (30 – 66 mg/kg) in comparison with the other sites (Table **2**). However, this was also the case with the fresh asphalt mass (45 mg/kg) (Table **2**). Higher PAH concentrations may thus be found in bitumen completely unexposed to any deicer chemical. The concentrations of individual PAHs did not differ in pavements of same origin exposed to different deicers (data not shown). These data and statistical analyses together point to deicers having no impact on PAH concentrations in the pavements.

Potential qualitative and quantitative changes in the patterns of aliphatic PHCs in the pavements exposed to different deicing agents were also studied. Within all the samples investigated, the concentrations of aliphatic PHCs ranged from 61 to 179 g/kg (Table **2**). The parallel samples from Hwy 6 and Helsinki airport had little variance between their aliphatic PHC concentrations (Table **2**). At Hwy 13 and Kuopio airport, the concentrations were much more variable (Table **2**). At Hwy 13, these variable concentrations were, however, indifferent to deicer chemical used (Table **2**). Furthermore, standard deviation between duplicate chemical analyses for individual samples was generally low for these samples (Table **2**). To conclude, this variance reflected the natural variation of aliphatic PHCs within bitumen. Qualitative assessment of the aliphatic PHCs neither revealed any significant changes between the samples exposed to NaCl or to KFo (Fig. **1**). The gas chromatographs of aliphatic PHCs were similar in samples exposed to NaCl or KFo or in the top or bottom layer within a site (data not shown).

Alatyppö *et al.* [8] suggested that heating up formate-containing asphalt pavement might result in changes in the concentrations of aliphatic and polyaromatic hydrocarbons in the bitumen’s maltene fraction. No evidence supporting this hypothesis was found in the present study. The concentrations of PAHs were indifferent to heat treatment (55 ^{o}C and 100 ^{o}C). Similarly, no qualitative changes could be seen in the chromatograms of aliphatic hydrocarbons due to the heat treatment (Fig. **2**). The concentrations of aliphatic hydrocarbons in the range C_{16} to C_{60} were statistically different between the samples but these differences were

Table 2. Concentrations of Aliphatic and Polyaromatic PHCs (per kg of Bitumen's Maltene Fraction) in Pavement Core Samples from the Airports of Helsinki and Kuopio, and Highways 13 and 6 at Suomenniemi and Taavetti, Respectively, and in Fresh Asphalt Mass. Layer (Top/Middle/Bottom) is Indicated

Site	Sample Code	Aliphatic PHCs (g/kg)			PAHs (mg/kg)		
		Top	Middle	Bottom	Top	Middle	Bottom
Helsinki	HV2	94±3[1]			21.7±0.0[1]		
	HV3	82±19[1]			21.5±3.0[1]		
	HV5	73±2[1]			14.2±0.3[1]		
	HV10	90±7[1]			18.1±0.2[1]		
	HV11	70±11[1]			17.6±3.4[1]		
	HVK1	88±45[1]			13.4±1.1[1]		
Kuopio	K2	69±10[1]			71.2±31.8[1]		
	K3	61±6[1]			342±73[1]		
	K6	119±17[1]			1411±1167[1]		
	K8	121±17[1]			2864±100[1]		
	K9	127±17[1]			1926±998[1]		
	K5	nd[2]	nd[2]	nd[2]	49.8	34.4	7768
	K7	nd[2]	nd[2]	nd[2]	65.8	30.1	5992
	KK2	158±14[1]			38.3±2.5[1]		
Hwy 13	SF2	102±4	-[3]	131±1	25.7±0.6	-[3]	10.4±1.0
	SF6	107±8	-[3]	130±0	15.1±1.6	-[3]	25.3±7.0
	SF10	113±6	-[3]	103±5	28.3±1.3	-[3]	14.0±0.4
	SS4	110±1	-[3]	142±3	20.5±1.9	-[3]	16.0±1.3
	SS8	93±13	-[3]	142±0	12.0±0.1	-[3]	11.7±1.1
	SS11	99±4	-[3]	179±16	23.5±0.3	-[3]	18.6±1.4
Hwy 6	TF1	66±2[1]			14.9[1]		
	TF3	70±2[1]			18.9±1.0[1]		
	TS2	71±9[1]			9.2±1.7[1]		
	TS4	74±0[1]			13.3±0.7[1]		
Fresh asphalt[4]	REF	154±4			45.0±8.8		

[1] aggregate sample where different layers were pooled and homogenized prior to analyses
[2] not determined
[3] the pavement core was divided into two parts
[4] sample was taken from the fresh asphalt mix upon the repaving of the Kuopio airport

attributed neither to any group of samples or deicer nor the heat treatment (Tables **3** and **4**). The observed changes in the concentrations thus provide additional piece of evidence that the measured differences reflect the natural variation of aliphatic hydrocarbons concentrations within pavements and batches of pavement mix.

For the analyses of aliphatic PHCs and PAHs, quality assurance measures were taken. In the extraction method, internal standards (*n*-hexadecane and 1,2,3-(CD)-indenofluoranthene) were used and their recoveries calculated. Yields of 100 ± 20 %, and 100 ± 40 % for *n*-hexadecane and 1,2,3-(CD)-indenofluoranthene, respectively, were set acceptable. The yields of the internal standards remained within these limits with the exception of 5 (out of 110) and 4 (out of 110) analyses for aliphatic PHCs and PAHs, respectively. In these cases, the samples appeared to contain small amounts of *n*-hexadecane and 1,2,3-(CD)-indenofluoranthene, respectively.

Table 3. Average Concentrations and Standard Deviations of Aliphatic and Polyaromatic PHCs in Sample Groups and Pairwise T-Test Between Groups' Average Concentrations. SF and SS Refer to KFo-Receiving and NaCl-Receiving Stretches on Hwy 13. HV Refers to Helsinki Airport

Sample Groups Compared in the t-test and Number of Samples Within the Group	**SF-Top/SS-Top n=8/n=8**		**SF-Bottom/SS-Bottom n=8/n=8**		**SF-Top / SF-Bottom n=8/n=8**		**SF 20°C/ SF 55+100 °C n=8/n=16**		**HV 20°C/ HV 55+100 °C n=6/n=6**	
Analyte	**PHCs[1]**	**PAHs**	**PHCs[1]**	**PAHs**	**PHCs[1]**	**PAHs**	**PHCs[1]**	**PAHs**	**PHCs[1]**	**PAHs**
Averages[2]	107.3/100.7	23.0/18.7	121.3/154.3	16.6/15.3	107.3/121.3	23.0/16.6	98.5/71.4	23.0/12.4	112.0/115.3	21.6/23.5
Standard deviations[2]	7.7/10.6	5.8/5.0	13.3/19.8	7.6/3.0	7.7/13.3	5.8/7.6	5.9/11.7	2.2/1.6	28.6/15.4	6.9/6.8
Reference value for the test estimate F[3] (average values)	2.2281	2.2281	2.2281	2.2281	2.2281	2.2281	2.0738	2.0738	2.2281	7.1464
Calculated value for the test estimate (average values)	1.2507	1.3914	3.3874	0.3726	2.2333	1.6591	3.0787	1.6393	0.2556	0.4818
Test result[3]	No	No	Yes	No	Yes	No	Yes	No	No	No

[1] aliphatic PHCs
[2] units: g/kg for aliphatic PHCs and mg/kg for PAHs
[3] Statistically significant difference between the averages compared.

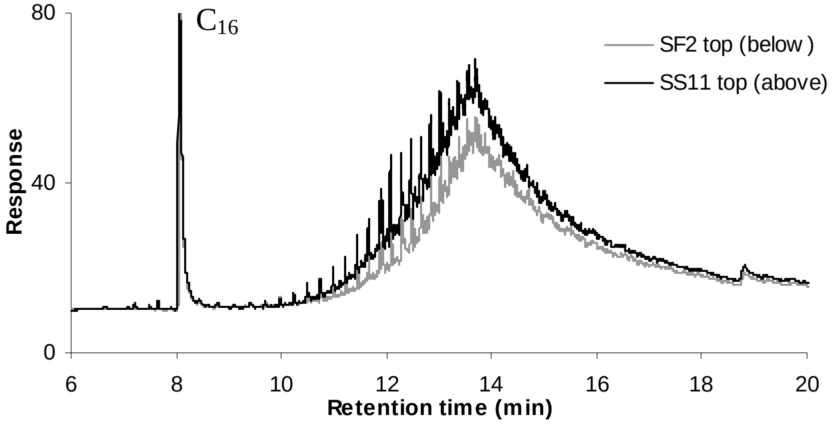

Fig. (1). Gas chromatogram of aliphatic PHCs in the range C$_{16}$-C$_{60}$ in asphalt pavement samples from Hwy 13. SF and SS refer to samples exposed to KFo and NaCl, respectively.

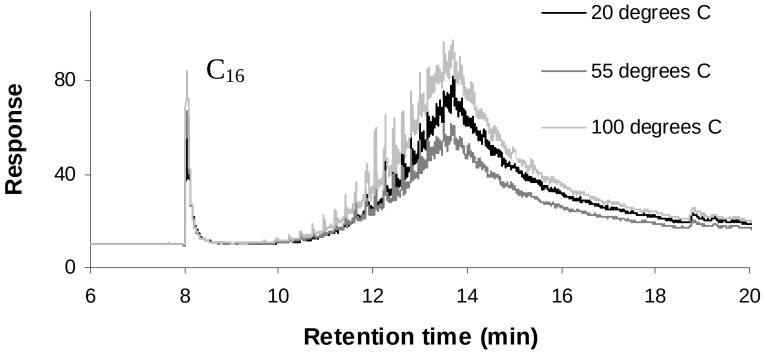

Fig. (2). Gas chromatogram of aliphatic PHCs in the range C$_{16}$-C$_{60}$ in asphalt pavement sample SF1 from Hwy 13 before (20 °C) and after a heat treatment up to 55 °C and 100 °C.

Residual Concentrations of Deicers in the Pavement and Pavement Hydraulic Conductivities

One of the issues addressed in the present study was the question to what extent deicing chemicals penetrate to asphalt pavements. For this purpose, concentrations of formate, acetate, and/or chloride were determined in the core samples from the 4 sites investigated. The samples were taken in early May, couple of weeks after the end of the deicing season. At Helsinki airport, where exclusively formate and acetate salts have been used as deicing agents for the past 15 years, formate and acetate concentrations ranged from 3.8 to 5.1 mg/kg and from 2.4 to 3.1 mg/kg, respectively, in the upmost pavement layer. In the bottom layer, the concentration ranges were 0.7–1.1 mg/kg and 0.5-0.9 mg/kg, respectively (Table **5**). In the core sample taken from an area with minimal to low exposure to deicers, no formate nor acetate was found (Table **6**). Overall, the amounts of deicers were thus low and they diminished with increasing depth at Helsinki airport. Similar trend was found at other sites investigated. Deicer concentrations were low and diminished with increasing depth. At Hwy 6, no formate was detected in any of the samples. At Helsinki airport, there was no residual formate and acetate in the reference core sample from the less or unexposed area (HVK3). At Kuopio airport, the reference sample from low to moderate exposure to deicers (KK2) seemed to contain equally much or even more formate and acetate than the actual samples.

The deicer concentrations detected in the core samples from different sites correlated with the loads of deicers applied at these sites. At Helsinki-Vantaa and Kuopio airports, strong correlation (0.997, $p<0.003$; Pearson) was found between the average annual mass of acetate and formate applied and the concentrations detected in the top pavement layer. In the highway samples such correlation could not be reliably calculated since formate concentrations were below detection limit at Hwy 6. However, formate concentrations were higher at Hwy 13, where KFo has been applied 2 years longer and at higher doses. The residual deicer concentrations in the pavement cores were generally higher at airports than at highways. Possible explanation to this may arise from the longer retention time of deicers at airports compared to that on highways.

The hydraulic conductivity of selected samples (n= 10) was also experimentally determined to further estimate the potential for deicer penetration into the pavements. In these tests, synthetic rain water, and water solutions containing 2.5 % (m/v) of NaCl or 5.0 % (m/v) of KFo were introduced through the pavement core samples using a hydraulic gradient of 50-60. Hydraulic conductivities ranged from 2.0 × 10^{-8} to 6.4 × 10^{-12} m/s in the pavement core samples (Table **4**).

Table 4. Water Permeabilities in Pavement Cores and the Concentrations of Aliphatic PHCs and PAHs Before and after a Heat Treatment. SF Refers to Hwy 13, and HV and HVK to Helsinki Airport

Sample (Saturation Solution)	Hydraulic Conductivity (m/s)	Aliphatic PHCs (g/kg)			PAHs (mg/kg)		
		20 °C[1]	55 °C	100 °C	20 °C[1]	55 °C	100 °C
SF9 (rain water)	1.1 x 10^{-9}	101±3	104±1	93±3	27.8±0.6	22.9±0.7	23.0±3.1
HV8 (rain water)	6.4 x 10^{-12}	159±3	146±3	141±4	28.4±0.7	28.3±0.6	28.5±1.6
HV4 (5-% KFo)	4.6 x 10^{-11}	106±3	100±7	nd[2]	26.6±0.9	29.7±4.0	nd[2]
HV6 (5-% KFo)	2.0 x 10^{-8}	101±7	112±8	nd[2]	26.1±0.0	26.1±1.1	nd[2]
HVK2 (5-% KFo)	2.1 x 10^{-11}	129±43	133±5	nd[2]	12.2±2.7	14.8±0.3	nd[2]
SF5 (2.5-% NaCl)	7.3 x 10^{-9}	1105±0	65±4	73±5	16.7±0.1	13.7±0.4	13.9±0.9
SF7 (2.5-%NaCl)	8.9 x 10^{-12}	101±6	87±12	85±3	11.6±0.6	10.5±1.9	10.2±0.2
SF1 (5-% KFo)	8.3 x 10^{-10}	58±0	58±8	77±1	11.6±1.5	11.9±0.5	13.7±0.8
SF3 (5-% KFo)	2.5 x 10^{-9}	96±2	65±1	61±3	14.9±0.1	12.8±1.2	12.7±0.9

[1] No heat treatment, sample kept at room temperature (20 °C).
[2] not determined

Table 5. Formate and Chloride Concentrations in Pavement Core Samples from Hwy 13 (at Suomenniemi) and Hwy 6 (at Taavetti) per kg of Bitumen's Malthene Fraction. SF and SS Refer to Samples Taken from the Stretch Deiced with Potassium Formate or with Sodium Chloride, Respectively. Pavement layer (Top/Bottom) is Indicated

Site	Sample	Formate (mg/kg)		Sample	Chloride (mg/kg)	
		Top	Bottom		Top	Bottom
Hwy 13	SF8	0.6±0.1	0.3±0.09	SS4	4.4±0.6	3.7±0.1
	SF12	0.5±0.04	0.3±0.1	SS8	3.4±0.3	8.1±0.6
Hwy 6	TF4	<0.2	<0.2	TS2	10.0	20.0
	TF6	<0.2	<0.2	TS6	9.8	6.9

Table 6. Concentrations of Formate and Acetate in Pavement Core Samples at Helsinki and Kuopio Airports per kg of Bitumen's Malthene Fraction. Samples HVK3 and KK2 were taken from the Least Deicer-Exposed Areas within the Airports

Site	Sample	Formate (mg/kg)			Acetate (mg/kg)		
		Top	Middle	Bottom	Top	Middle	Bottom
Helsinki	HV2	3.8±0.2	-[1]	0.7±0.1	2.4±0.03	-[1]	0.5±0.3
	HV5	5.1±0.1	-[1]	1.1±0.2	2.8±0.1	-[1]	0.9±0.1
	HV10	4.8±0.3	-[1]	0.9±0.3	3.1±0.2	-[1]	0.6±0.2
	HVK3	<0.2	-[1]	<0.2	<0.2	-[1]	<0.2
Kuopio	K3	1.1±0.3	0.6±0.4	0.4±0.3	2.2±0.8	0.6±0.2	0.6±0.2
	K8	2.6±1.5	1.3±0.6	1.6±0.02	2.0±1.1	0.8±0.4	1.4±0.1
	KK2	2.6	-[1]	2.0	1.5±0.1	-[1]	1.4

[1] only two layers existed.

The obtained values are typical for asphalt pavements with 3-5 % void space and deicing history or solution used in the tests had no impact on the rates measured. The low concentrations of deicers in the pavements thus reflect the character of asphalt pavements studied; they are low-permeable materials to which deicer-containing water solutions penetrate mostly due to slow diffusion processes.

CONCLUSIONS

In the current study, the possible changes in the quantity and quality of aliphatic PHCs and PAHs in the maltene fraction of bitumens from asphalt pavements exposed to various deicing agents. Whether heating up formate-containing samples would promote changes in the above chemical constituents was also investigated in laboratory conditions. To estimate potential for such reactions in pavements *in situ*, deicer concentrations and water permeabilities were determined for samples taken shortly after the end of a deicing season.

This work provided evidence that deicing agents (NaCl, acetate- and formate salts) do not have any impact on the quality or quantity of aliphatic PHCs or PAHs and these impacts could not be artificially induced in laboratory heating experiments. No evidence for actual pavement failures or on-going damage process was found in the pavement samples from two airports and two highways in Finland, where formate and/or acetate deicers are used.

ABBREVIATIONS

C_{10} = Decane $C_{10}H_{22}$
C_{16} = Hexadecane $C_{16}H_{34}$
C_{40} = Tetracontane $C_{40}H_{82}$
C_{50} = Pentacontane $C_{50}H_{102}$
C_{60} = Hexacontane $C_{60}H_{122}$
HPLC = High performance liquid chromatography
KFo = Potassium formate
nd = Not determined
PAH = Polyaromatic hydrocarbon
PHC = Petroleum hydrocarbon

ACKNOWLEDGEMENTS

We are grateful to Finnish Road Administration (EKOTULI theme) and to Finavia for funding this study and to Katri Eskola and Tuija Hänninen from Finnra and Finavia, respectively, for their valuable input throughout the project. We also thank Jukka Rinkinen and Kirsi Rosendahl for their excellent technical help with the organic chemical analyses.

REFERENCES

[1] F. M. D'Itri, Ed., *Chemical deicers and the environment*, Chelsea; Lewis Publishers, 1992.

[2] P. P. Hellstén, J. M. Salminen, K. S. Jørgensen and T. H. Nystén. "Use of potassium formate in road winter deicing can reduce groundwater deterioration", *Environ. Sci. Technol*., vol. 39, pp. 5095-5100, July 2005.

[3] X. Shi, L. Fay, C. Gallaway, K. Volkening, M. M. Peterson, T. Pan, A. Creighton, C. Lawlor, S. Mumma, Y. Liu and T. A. Nguyen, *Evaluation of alternative anti-icing and deicing compounds using sodium chloride and magnesium chloride as baseline deicers – Phase I. Report No. CDOT-2009-1*. Colorado Dept. of Transportation, DTD Applied Research and Innovation Branch. Available at http://cospl.coalliance.org/fez/es-erv/co:5166/tra-210091internet.pdf [Accessed Jan 10, 2011]

[4] C. Amrhein, J. E. Strong and P. A. Mosher, "Effect of deicing salts on metal and organic matter mobilization in roadside soils", *Environ. Sci. Technol.*, vol. 26, 703-709, Apr. 1992.

[5] P. Hellstén and T. Nystén. "Migration on alternative deicers in unsaturated zone of aquifers - *in vitro* study", *Water Sci. Technol.*, vol. 48, pp. 45-55, Sept 2003.

[6] Y. Hassan, A. O. Abd El Halim, A. G. Razaqpur, W. Bekheet and M. H. Farha, "Effects of runway deicers on pavement materials and mixes: Comparison with road salt", *J. Transport. Eng*., vol. 128, pp. 385-391, July/Aug 2002.

[7] X. Shi, M. Akin, T. Pan, L. Fay, Y. Liu and Z. Yang. "Deicer impacts on pavement materials: Introduction and recent developments", *Open Civil Eng. J*., vol. 3, pp.16-27, 2009.

[8] V. Alatyppö, P. Jauhiainen and J. Valtonen, *Conclusions—Finnish Deicing Project.* Helsinki University of Technology, Laboratory of Highway Engineering, Espoo, Finland. [Online] Available at

http://www.tkk.fi/Yksikot/Rakennus/Tie/Julkaisut/PDF/ATT00056.pdf [Accessed Nov 15, 2010]

[9] T. Hänninen, personal communication, Sept 2009.

[10] J. J. Kolak and R. C. Burruss, "An Organic Geochemical Assessment of CO_2-Coal Interactions During Sequestration", U.S. Geological Survey Open-File Report 03-453. Poster presentation in the *Second Annual Conference on Carbon Sequestration*, Alexandria, Virginia, 2003.

[11] J. Yan, X. You, X. Li, M. Ni, X. Yin and K. Cen, "Performance of PAHs emission from bituminous coal combustion". *J Zhejiang University Sci.*, vol. 5, pp.1554-1564, 2004.

Received: November 25, 2010 Revised: January 12, 2011 Accepted: January 20, 2011