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Emission characteristics of VOCs from athletic tracks

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Abstract

Dynamic and flow-through flux chambers are convenient tools for field measurements of gas or VOC emission flux from solid surfaces in the field. This study was undertaken to collect on site and quantify the emissions of volatile organic compounds (VOCs) released from athletic running tracks. Three typical types of tracks, one synthetic rubber and two tracks (types I and II) consisting mainly of polyurethane, were studied. They were all installed with adhesives and backings, both of which contributed significant amount of VOCs. VOCs released from the track surface were collected with a flux chamber and subsequently analyzed by a gas chromatograph/mass spectrometer (GC/MS). Also, for each track and at each selected time the emission flux and mass emission were measured on site under outdoor conditions over a period of 40 min. GC/MS analyses show that the VOCs emitted include 2-methyl furan, butanal, methyl ethyl ketone, benzene, heptane, methyl isobutyl ketone, toluene + octane, hexanal, nonane + ethylbenzene, xylenes + styrene, propyl benzene, decane, 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene, 1,2,3-trimethyl benzene and undecane. Of these, hexanal was the common and principal compound for all three types of tracks. 2-Methyl furan and methyl isobutyl ketone were the characteristic compounds for the synthetic rubber and the type II of polyurethane tracks, respectively. In the field studies, no unique compounds were found in the type I of polyurethane tracks. For each of these three types of tracks the total-VOCs emission flux was correlated to the track age and track surface temperature. The results of multiple regression analysis showed good correlation. The type II polyurethane track had the highest decay rate, while the synthetic rubber track had the lowest decay rate. Two years after the track installation, the VOC concentrations

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measured at 1.5 m above the track, the breathing height of school children, were not significantly higher than the background levels. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past few years, emissions of volatile organic compounds (VOCs) from the synthetic athletic tracks into the atmosphere are becoming a growing concern in Taiwan. According to reports [1,2], a variety of VOCs, including benzene, toluene, xylenes, ethylene glycol, iso-butyl alcohol, methyl ethyl ketone, acetone, etc. are probably involved in manufacturing raw materials of the sport tracks or used during track installation. Therefore, many members of the Taiwan legislative assembly strongly queried the potential threat of the tracks to the health of school children and possible adverse effects on the environment. This research institute was commissioned by the City Government of Kaohsiung to do a thorough investigation in order to determine the nature and extent of the emission.

Up till now, little qualitative and quantitative information has been reported on the emissions of VOCs from athletic tracks in Taiwan or in other countries. The only known project (sponsored by the Taipei City Government, Taiwan) made a limited qualitative study on polyurethane (PU) tracks [3]. In that project, samples cut out from actual PU tracks were sliced into small stripes, which were irradiated with ultraviolet rays in a simulated environment at 60°C for one week, extracted with a solvent, and then analyzed by high performance liquid chromatography (HPLC). However, no further compound identification and quantification either by liquid chromatograph/mass spectrometry (LC/MS) or GC/MS was attempted. In addition, the emission rate or flux of VOCs was not studied.

Since some of the VOCs emitted from synthetic athletic tracks may be toxic and hence pose health hazard to the public, it is important to identify the VOCs and to quantify their concentration levels. This study, commissioned by the Bureau of Education, Kaohsiung City Government, Taiwan, was undertaken to do on-site investigations and to measure the emission fluxes and mass emission rates of VOCs released by major typical tracks used in Taiwan.

Also, in order to understand the long-term fate of VOCs in athletic tracks, a mathematical model describing how the emission rate is affected by time and track age was developed. In addition, the VOC concentrations at the breathing height of school children (1.5 m above the track) were measured.

2. Experimental

2.1. Athletic running tracks

Based on preliminary comparisons on all tracks used in schools of Kaohsiung City for their materials, gas permeability and installation methods, 19 tracks investigated in

this study were grouped according to their nature into three types — (1) polyurethane type I (PU-I), (2) polyurethane type II (PU-II) and (3) synthetic rubber (SR). They are described in detail in Table 1. The selected tracks were generally representative of those used in local schools. Track PU-I consisted of polyols and polyisocyanates, which were mixed at the site at a specific ratio and then embedded with PU granules. Track PU-II, while similar to Track PU-I, was embedded with ethylene propylene diene monomer (EPDM) rubber granules. Track SR was manufactured in the form of rolled sheets and was installed at the site with adhesives. Due to their structure and materials used, Tracks PU-II and SR are expected to have higher gas permeability.

2.2. Flux chamber method

Dynamic flux chambers have been widely used as convenient tools for measuring gas emissions from landfills, surface impoundment, natural sediments, chemical spill sites, and so forth. The above-mentioned use, design and testing of this kind of chamber are discussed in detail elsewhere [4–11]. Briefly, a controlled flow of clean, dry sweeping nitrogen is introduced into the open-bottom flux chamber at a constant, pre-determined rate. Gas samples are each collected with an adsorption tube at the outlet of the open-bottom chamber, which is temporarily sealed to the track surface prior to sampling. VOCs collected in the adsorption tubes are then analyzed by a GC/MS. The design of the chamber is a modified version of the one used by Gao et al. [10]. Fig. 1 shows the schematic details of the flux chamber used in this study. VOCs flux from the track surface is calculated from the observed concentration difference between the inlet and the outlet air and the overall flow rate through the dynamic flux chamber:

$$J = \frac{Q(C_{out} - C_{in})}{A} \tag{1}$$

where J is the emission flux of VOCs in $\mu g \; m^{-2} \; h^{-1}$; Q is the controlled constant flow rate of air through the chamber ($0.0150 \; m^3 \; h^{-1}$); A is the top surface area of the enclosed track ($0.1004 \; m^2$); C_{in} and C_{out} are the spatial average or representative

Table 1
Descriptions of the three types of athletic tracks

| Parameters	Tracks		
	PU-I	PU-II	SR
Track materials	PU, PU granules	PU, EPDM granules	synthetic rubber
Permeability for gas	Bad	good	greater than PU-I
Typical installation	coating, curing	coating, curing	glue-down
Form	liquid	liquid	rolls
Backing adhesive	NS[a]	NS[a]	NS[a]
Track thickness	12–15 mm	12–15 mm	12–15 mm
Track age	23–87 months	10–61 months	14–114 months
The number of tracks	5	9	5

[a] NS: not specified by manufacturer.

(a)

(b)
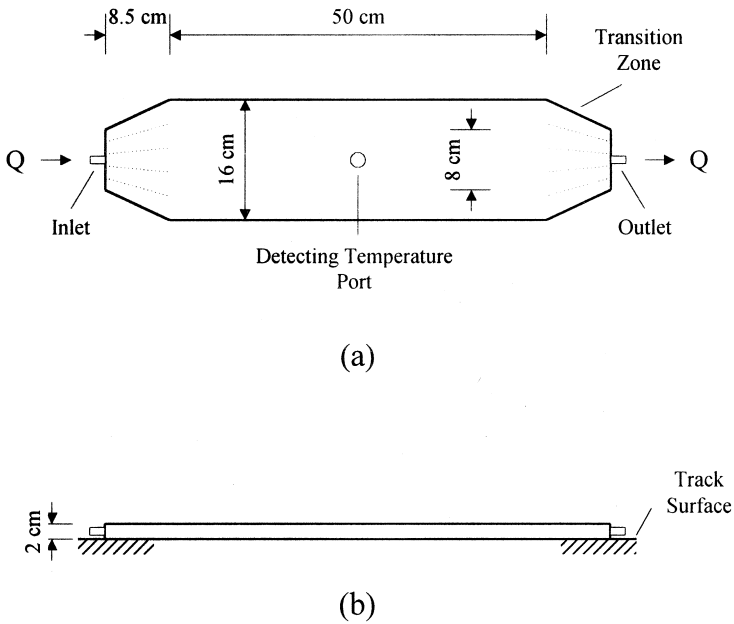
Fig. 1. Schematic diagram of the dynamic flux chamber system: (a) top view, (b) side view (scale = 1:10).

concentrations of the target gas in $\mu g \ m^{-3}$ in the in-coming air at the inlet and in the exiting air at the outlet, respectively.

When clean and high purity nitrogen is used as the sweep gas, $C_{in} = 0$ and the above equation can be rewritten as:

$$J = \frac{QC_{out}}{A}.$$

(2)

Several factors, including chamber size and volume, material of chamber construction, sampling time and sweep air flow rate, can affect the performance of sample collection. They have been considered and discussed in other papers [6,7,10,28,29].

The sensitivity of the flux chamber method is not dependent on the chamber size or volume. In practice, however, the choice of chamber size is determined by several considerations [28]. On the one hand, the surface area enclosed should be as large as feasible so that the measured emission flux is not over-biased by relatively small areas of unrepresentative emissions. On the other hand, the chamber should be small enough so that it is lightweight, easy to transport and simple to use. Compared to other emission sources, the track surface studied is considered as having a relative uniform emission source. Therefore, we chose to use a smaller chamber.

The evaluation of two points are necessary when selecting construction materials for a dynamic flux chamber: (1) adsorption or emittance of gas species from the chamber and auxiliary equipment; and (2) changes in the net energy flux at the sampling location due to the chamber [28]. The base of the dynamic flux chamber is stainless steel and the

sampling lines are made of Teflon with stainless steel fittings. The contribution from the chamber internal surface itself to the VOC signal is measured by sealing the chamber bottom to a clean piece of glass and sampling outlet VOC concentrations over time periods comparable to those used over tracks. The VOC signal decrease caused by the sampling system was also determined as previously mentioned. In all cases, no problem was found in both the blank tests and the recovery tests. Track surface temperature is also measured inside the chamber during all flux measurements. When the sun is high over the horizon and the weather is hot, the temperature increase may be over 10°C.

The minimum sampling time necessary is defined as the time required to approach a steady-state concentration within the chamber. It has been reported that to reach a steady-state concentration it typically takes three to four residence times, which is defined as the chamber volume divided by the sweep air flow rate. After the steady-state concentration is reached, sampling can be initiated [28]. The maximum acceptable sampling time depends on the nature of the emission source and the objectives of the monitoring program. Long-duration sampling will nullify the results of sorbent-based sampling techniques.

Studies using different flux chamber designs have shown varied results concerning the effects of the sweep air flow rate on emissions: no effect, an increase in emission rate with sweep air flow rate, and even an increase in emission rate with a lower sweep air flow rate [7,28,30,31]. Emission sources discussed in the above-mentioned articles include: municipal solid waste landfills, a subsurface contamination covered by clean soil, contaminated surface soils, a quiescent liquid surface with dissolved contaminants, a quiescent liquid surface with a floating organic layer, and an aerated liquid surface. However, those emission sources are characterized by evaporation. We must point out that the athletic tracks investigated in this study are quite different from other emission sources because their emissions are likely to be characterized by internal diffusion. Bortoli et al. [29] have proved that the influence of air velocity on the emission rate of VOCs is negligible for sources characterized by internal diffusion (e.g., PVC tile), but strong for sources characterized by evaporation.

The operating conditions for the used dynamic flux chamber are described in Table 2.

2.3. Preliminary study

Among the 19 investigated tracks three relatively newer ones, which had track ages of 23, 10, and 14 months, respectively, were selected to represent three types of tracks

Table 2
Conditions specified for the operation of the flux chamber

Parameters	Flux chamber
Chamber internal volume, cm^3	2008
Track surface temperature, °C	33.1–52.3
Sampling duration, min	40
Sweep air flow rate, ml/min	250
Residence time, min	8
Equilibrium time, min	30
Sampling volume, l	10

(PU-I, PU-II and SR), and they were first studied to determine the chemical identities of the major VOCs in the emissions.

The sampling system, including a cylinder of high purity nitrogen, two mass flow controllers, a flux chamber, a sampling pump and Tedlar® bags required to measure gas emissions, is schematically shown in Fig. 2. Using a mass flow controller located in front of the chamber, high purity nitrogen was introduced at a steady rate of 250 ml/min into the chamber. Before the chamber was placed on the track surface, the sampling lines and chamber were purged. The chamber was then sealed to the track surface while the sweep gas was kept flowing. At the time the chamber was sealed to the track the time was recorded. After 30 min, the sample collection was initiated. The exiting gas was drawn into the 10-l Tedlar® bag (Model 232-08, SKC) by a sampling pump (Model AirCon2, Gillian), whose flow rate was maintained at 250 ml/min by a second mass flow controller located between the chamber and the sampling pump.

VOC concentrations in the exiting gas were determined by analyzing the gas samples previously collected in 10-l Tedlar® bags. These gas samples were first concentrated and thermally desorbed with an AERO Trap Desorber (Model 6000, Tekmar), then introduced into a capillary gas chromatograph/mass spectrometer (Model 5890 Series II Plus GC plus a Model 5972 Series MS, Hewlett-Packard). The results of the preliminary studies provided an estimate of the chemical identities of the major VOCs found in all three types of synthetic tracks.
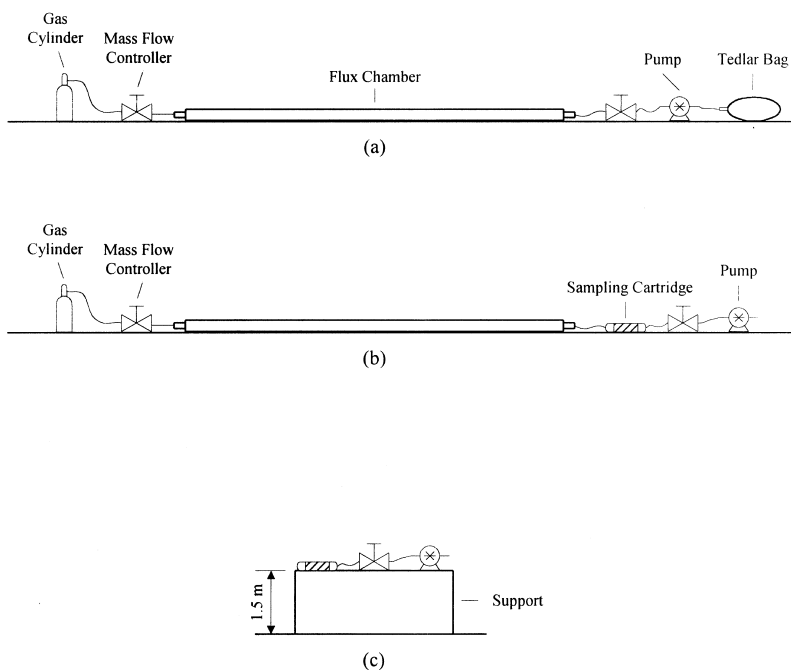

Fig. 2. VOCs sampling system (not to scale): (a) preliminary study, (b) field study, and (c) breathing height.

2.4. Field study

In the field studies, we collected the gas samples released by the tracks directly from the track surfaces at 19 selected schools located in Kaohsiung City. Five samples of Track PU-I, nine samples of Track PU-II, and five samples of Track SR were taken, respectively.

Based on the results of previous screening measurements, considerations of economic, time and toxicity of compounds, 23 target VOCs were chosen for quantitative analyses in field studies. Furthermore, we followed Eklund's [28] sampling strategy, in which minimums of 10% of the sampling points were sampled in duplicate. Therefore, we only double sampled for the three newer tracks, previously mentioned in Section 2.3, not for every investigated track. Optimization tests of the Tenax tubes, done with double sampling, showed that the sampling duration of 40 min at a constant flow rate of 250 ml/min was the optimal condition.

The sampling devices (shown in Fig. 2) and sampling procedure employed in the field studies are similar to those used in the preliminary studies. However, for the field studies VOC samples were collected with adsorption tubes (Perkin Elmer), each packed with 250 mg Tenax-TA (60/80 mesh). After sampling, the used Tenax-TA tubes should be stored immediately in a freezing container and promptly shipped back to the laboratory for analysis. Also, an automatic thermal desorption system (Model ADT-400, Perkin Elmer) was used instead during GC/MS analyses.

2.5. Flux correlation

Factors that affect the emission behaviors of semi-volatile or volatile organic compounds (SVOCs or VOCs) from matrix surfaces include: vapor pressure, matrix adsorption, Henry's law constant, diffusion coefficients, surface and ambient temperatures, time, and relative humidity, along with other conditions and properties that control movement of VOCs away from matrix surfaces [11–19]. In recent years, many investigators have attempted to correlate SVOC or VOC volatilization with these various influencing factors in descriptive equations that can be used to predict emissions from matrix surfaces. These equations or models range in complexity from the ''effusion'' type (e.g. Knudsen effusion equation [14]), which assumes that volatilization occurs from a non-adsorptive surface or from a well-mixed body of water, to more descriptive equations that include all possible factors that together will significantly affect net volatilization [15,20–24]. In this study we developed a simple mathematical model which includes only two readily measurable parameters — track surface temperature and track age. Literature supporting our views is discussed later.

2.6. VOC concentrations at breathing height

The three newer tracks, mentioned previously in Section 2.3, were located in rural or suburban sites. These sites were tested for VOC concentrations at breathing height at two different elevated positions, above the tracks and far away from the tracks. Each elevated position was tested in several places. Three samples (one sample for each track)

were taken at 1.5 m above the tracks in the middle of straight central lanes. Three more samples (one sample for each track) were taken at 1.5 m above the ground at sites that were at least 50 m away from tracks, streets or any possible VOC source. A supporting stand 1.5 m in height was used to hold a sampling pump, a mass flow controller and adsorption tubes. A schematic diagram is given in Fig. 2. Samples were collected with adsorption tubes, each packed with 250 mg Tenax-TA (60/80 mesh). A mass flow controller maintained the sampling flow at a steady rate of 250 ml/min. The ambient air was drawn through the adsorption tubes with a sampling pump and a mass flow controller. Six samples were collected, stored, shipped and analyzed by GC/MS, as described above.

3. Results and discussion

3.1. Preliminary study

A variety of VOCs were detected in the preliminary study, 36 of which, as listed in Table 3, were identified by matching their mass spectra with those in the databases (HP-G1030C MS ChemStation with NIST MS Library).

These VOCs were either used in production of PU or generated from within the track after installation. The major VOCs include methyl ethyl ketone, methyl isobutyl ketone, benzene, toluene, xylenes, hexanal, and more.

In the preliminary studies propylbenzene was found to be unique to the type I of PU tracks. Therefore, Table 3 accurately shows the results gathered from the preliminary studies. Yet upon more extensive research in the field studies, the propylbenzene found in Track PU-I was not a unique chemical compound to Track PU-I, since all three types of tracks had trace amounts of propylbenzene.

A comparison with other similar emission sources (new carpets) showed that the species of VOCs emitted by athletic tracks, older than 10 months, were totally different from those emitted by new carpets investigated in Hodgson's [19] study with the exception of the emission of styrene and undecane. In Hodgson's research, formaldehyde, vinyl acetate, 2,2,4-trimethylpentane, 1,2-propanediol, styrene, 4-phenylcyclohexene and 2,6-di-tert-butyl-4-methylphenol were major emittant from new carpets.

The most abundant 23 VOCs were chosen from the above-mentioned 36 VOCs for quantitative analyses in the subsequent field studies.

3.2. Species of VOCs emitted by tracks

In total, 19 VOCs were quantified in field studies. A few compounds, including methylene chloride, hexane, chloroform, 1-octene, were not quantified because their concentrations were far below the limits of quantitation.

The major compounds emitted by Track PU-I, PU-II and SR, based on the results of the field studies, are listed in Table 4. Track PU-I emitted primarily hexanal, toluene +

Table 3
Thirty-six VOCs emitted from Tracks PU-I, PU-II, and SR in the preliminary studies

No.	Compounds	Tracks		
		PU-I	PU-II	SR
1	1-heptene			a
2	1-octene			a
3	2-propenal, 2-methyl			a
4	4-pentenal		a	
5	acetaldehyde			a
6	benzene	a	a	a
7	m-xylene	a	a	a
8	benzene, 1-ethyl-2-methyl	a	a	a
9	benzene, 1-ethyl-3-methyl	a	a	a
10	benzene, 1-ethyl-4-methyl		a	
11	benzene, 1,2,3-trimethyl	a	a	
12	benzene, 1,2,4-trimethyl		a	
13	benzene, 1,3,5-trimethyl	a	a	
14	benzene, propyl-	a		
15	butanal		a	
16	butane			a
17	cyclohexane	a	a	
18	decane			a
19	ethylbenzene	a	a	a
20	furan	a	a	a
21	heptane			a
22	hexanal	a	a	a
23	hexane			a
24	methyl ethyl ketone			a
25	methyl isobutyl ketone		a	
26	nonane			a
27	octane			a
28	o-xylene	a	a	a
29	oxirane		a	
30	p-xylene	a	a	a
31	propane	a	a	
32	propene		a	
33	styrene			a
34	toluene	a	a	a
35	undecane	a	a	
36	furan, 2-methyl			a

[a] Indicates compounds emitted by this type of track.

octane and xylenes + styrene. The dominant compounds emitted by Track PU-II were hexanal, methyl isobutyl ketone and xylenes + styrene. The dominant compounds emitted by Track SR were hexanal, 2-methyl furan and toluene + octane. Of these, hexanal was the principal compound common to all three types of tracks. Methyl isobutyl ketone and 2-methyl furan were the characteristic compounds for Track SR and Track PU-II, respectively. In the field studies, no chemical compound was found unique to Track PU-I.

Table 4
VOCs emitted by Track PU-I, PU-II and SR in field studies (measured by the flux chamber)

Compounds	Track types		
	PU-I	PU-II	SR
Furan, 2-methyl		+[a]	+ + +[c]
Butanal		+	
Methyl ethyl ketone		+	
Benzene	+	+	+
Heptane	+	+	+
Methyl isobutyl ketone		+ + +	
Toluene + octane	+ + +	+	+ +[b]
Hexanal	+ + + +[d]	+ + + +	+ + + +
Nonane + ethylbenzene	+	+	+
Xylenes + styrene	+ +	+ +	+
Benzene, propyl	+	+	+
Decane		+	+
Benzene, 1,3,5-trimethyl	+	+	
Benzene, 1,2,4-trimethyl	+	+	+
Benzene, 1,2,3-trimethyl	+	+	
Undecane	+	+	

[a] +: Present in sample.
[b] + +: Third most abundant compound.
[c] + + +: Second most abundant compound.
[d] + + + +: The most abundant compound.

3.3. Total VOCs emission flux from athletic tracks

The following equation, rewritten from Eq. (2), was used to define the emission flux of VOCs:

$$J = \frac{W}{At} \tag{3}$$

where J is the emission flux of VOCs in $\mu g\ m^{-2}\ h^{-1}$, W is the total mass (μg) of collected VOCs during the sampling period t (h), and A is the track area (m^2) enclosed by the flux chamber.

The emission fluxes of the target compounds for the investigated tracks are summarized in Table 5. For tracks which were less than 2 years old, the ranges of total-VOC (TVOC) emission fluxes were 7.3, 6.6–18.8 and 8.3–11.8 $\mu g/m^2$ h, with averages of 7.3, 9.4 and 9.9 $\mu g/m^2$ h, respectively, for PU-I, PU-II and SR. For tracks older than 2 years, the ranges of TVOC emission fluxes were 0.6–5.5, 1.0–5.6 and 0.1–4.9 $\mu g/m^2$ h, with averages of 3.1, 3.8 and 1.7 $\mu g/m^2$ h, respectively, for PU-I, PU-II and SR.

Clearly, all TVOC emission fluxes from three types of tracks were found to decay with track age, which was logical. Again, the larger average emission fluxes for Track PU-II and SR were possibly due to their higher gas permeability. That would also explain why the reduction in emission fluxes for Track PU-II and SR were faster than Track PU-I over the same time periods.

Table 5
VOC emission fluxes of tracks (μg m^{-2} h^{-1})

Compound	PU-I $\leq$ 2 yr.[a]		PU-I $>$ 2 yr.[b]		PU-II $\leq$ 2 yr.		PU-II $>$ 2 yr.		SR $\leq$ 2 yr.		SR $>$ 2 yr.	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Furan, 2-methyl	N.D.	N.D.	N.D.	N.D.	N.D.–0.3	N.D.	N.D.	N.D.	2.8–4.2	3.5	N.D.–0.8	0.4
Butanal	N.D.	N.D.	N.D.	N.D.	N.D.–1.5	0.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Methyl ethyl ketone	N.D.	N.D.	N.D.	N.D.	N.D.–0.5	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzene	0.1	0.1	N.D.–0.2	0.1	N.D.–0.2	0.1	N.D.–0.2	N.D.	0.2–0.3	0.2	N.D.–0.1	N.D.
Heptane	N.D.	N.D.	N.D.–0.3	0.1	N.D.–0.4	0.1	N.D.	N.D.	N.D.–0.2	0.2	N.D.	N.D.
Methyl isobutyl ketone	N.D.	N.D.	N.D.	N.D.	0.4–7.3	2.8	N.D.–1.5	0.7	N.D.	N.D.	N.D.	N.D.
Toluene + octane	0.9	0.9	N.D.–0.8	0.5	0.1–0.5	0.4	N.D.–0.5	0.2	N.D.–1.1	0.5	N.D.–0.4	0.1
Hexanal	2.1	2.1	0.3–1.7	1.3	2.2–6.1	4.1	0.8–3.1	2.1	3.3–5.7	4.5	N.D.–3.2	1.2
Nonane + ethylbenzene	0.6	0.6	N.D.–0.3	0.2	0.2–0.7	0.4	N.D.–0.5	0.2	0.1–0.3	0.2	N.D.	N.D.
Xylenes + styrene	0.6	0.6	0.2–0.8	0.5	0.2–0.9	0.6	0.1–0.6	0.4	0.2–0.7	0.4	N.D.–0.2	N.D.
Benzene, propyl	N.D.	N.D.	N.D.–0.3	N.D.	N.D.–0.2	N.D.	N.D.–0.2	N.D.	0.2–0.6	0.4	N.D.–0.1	N.D.
Decane	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.–0.3	0.1	N.D.–0.1	N.D.	N.D.	N.D.
Benzene, 1,3,5-trimethyl	0.3	0.3	N.D.–0.2	N.D.	N.D.–0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzene, 1,2,4-trimethyl	0.5	0.5	N.D.–0.6	0.3	0.2–0.8	0.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzene, 1,2,3-trimethyl	0.2	0.2	N.D.–0.2	N.D.	N.D.–0.5	N.D.	N.D.–0.4	0.2	N.D.–0.2	N.D.	N.D.–0.2	N.D.
Undecane	1.8	1.8	N.D.–0.7	0.2	N.D.–0.2	N.D.	N.D.–0.1	N.D.	N.D.	N.D.	N.D.	N.D.
Total-VOCs	7.3	7.3	0.6–5.5	3.1	6.6–18.8	9.4	1.0–5.6	3.8	8.3–11.8	9.9	0.1–4.9	1.7

[a] $\leq$ 2 yr.: Track age not more than two years.
[b] $>$ 2 yr.: Track age more than two years.

Table 5, which presents the VOC emission fluxes for athletic tracks, seemed to show lower VOC emission fluxes than those of new carpets [19]. In fact, it was true that new carpets (new born carpets) could emit 1 to 2 orders higher VOC concentrations (on a styrene basis) than our investigated tracks could. But the interesting phenomenon was that the styrene emission fluxes for new carpets, after 7 days of use, lowered to the same level as those of athletic tracks. Hodgson's study showed two important results: (1) for
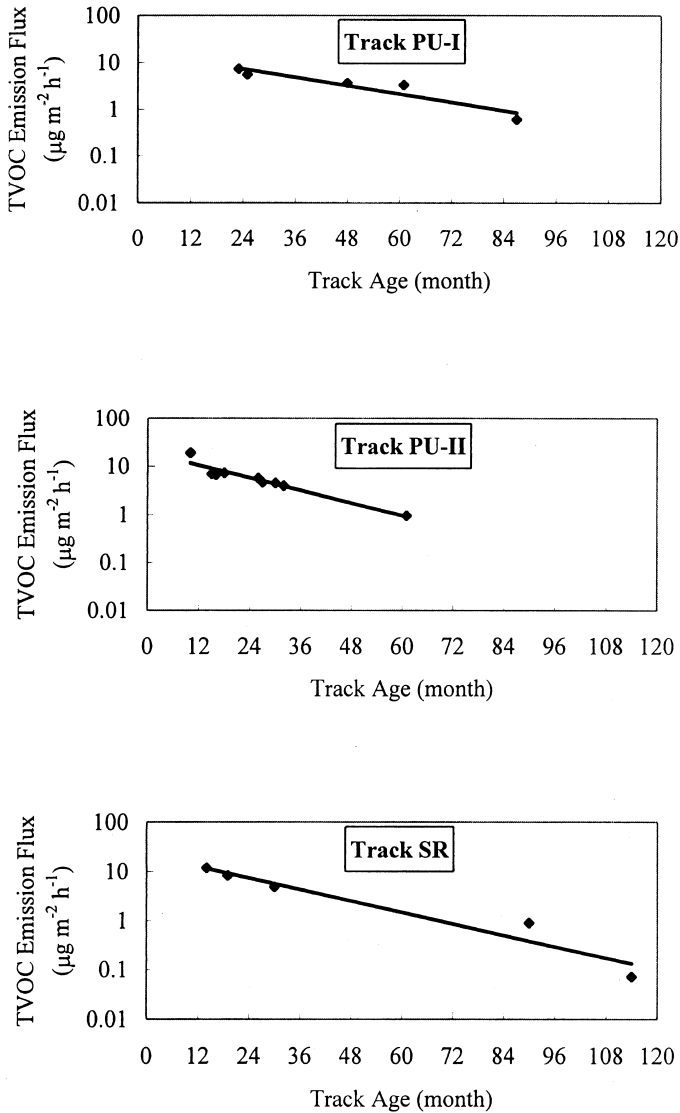
Fig. 3. Track TVOC emission fluxes vs. track age for each type of track.

Table 6
Correlation of total VOCs emission flux to track age

Tracks	$J = F(t)$	R_a^2	Number of tracks
PU-I	$J = 11.86 e^{-0.025\,t}$	0.8909	5
PU-II	$J = 38.94 e^{-0.089\,t}$	0.7799	9
SR	$J = 25.26 e^{-0.056\,t}$	0.9884	5

J = TVOCs emission flux ($\mu g\ m^{-2}\ h^{-1}$).
t = track age (month).
R_a^2 = adjusted coefficient of multiple determination.

styrene, formaldehyde and TVOC the fractional reductions in the emission rates that occurred from 24 to 168 h were 90%–94%, 68% and 61%–76%, respectively, and (2) the chamber concentrations of most compounds decreased rapidly over the first 12 h of the experiments and the decay coefficients were generally related to compound volatility, with the most volatile compounds having the most rapid decay.

Therefore, this evidence implies that athletic tracks might emit something toxic and unhealthy for people during the period of track installation and continuously for a short period following track installation. Unfortunately, we did not have the opportunity to measure emissions during track installation and after track installation in this study.

3.4. Flux correlated to track age and track surface temperature

Carpet age has already been shown to be an important factor affecting carpet VOC emissions in Hodgson's [19] study. Based on Hodgson's results, we also assumed that the TVOCs emission flux of track should decay exponentially over the track age, which could be expressed as Eq. (4):

$$\ln J = -kt + \text{const} \tag{4}$$

where k is the track age coefficient.

The TVOC emission flux of each track was correlated with the track age in a $\log_e$ flux/time plot for each track (Fig. 3), which resulted in the following correlations (Table 6).

Table 7
Correlation of total-VOC emission flux to track age and surface temperature. J = TVOCs emission flux ($\mu g\ m^{-2}\ h^{-1}$). t = track age (month). T = track surface temperature (K). R_a^2 = adjusted coefficient of multiple determination

Tracks	$J = F(t,T)$	R_a^2
PU-I	$J = 1.48 \times 10^6 e^{-0.021t}\ e^{-3678.2/T}$	0.9026
PU-II	$J = 1.60 \times 10^7 e^{-0.057t}\ e^{-4303.4/T}$	0.7951
SR	$J = 2.01 \times 10^3 e^{-0.061t}\ e^{-1352.6/T}$	0.9871
All-Tracks[a]	$J = 7.00 \times 10^3 e^{-0.055t}\ e^{-1808.1/T}$	0.8137

[a]All-Tracks: All nineteen tracks pooled together.

As our observations and expectations, the regression analysis for TVOCs emission flux of each track against the track age has shown that exponential curves exhibited very good correlation between flux and track age except for Track PU-II. The main reason for poor correlation for Track PU-II is that data obtained from different and separate tracks with various track ages and under diverse surface temperatures were pooled together.

Furthermore, track surface temperature has been shown to have some correlation to SVOC or VOC emissions from treated matrix. Despite the strong correlation with track age noted above, our data suggested that track surface temperature was another factor affecting TVOC emission flux. The relationship between TVOC emission flux of track
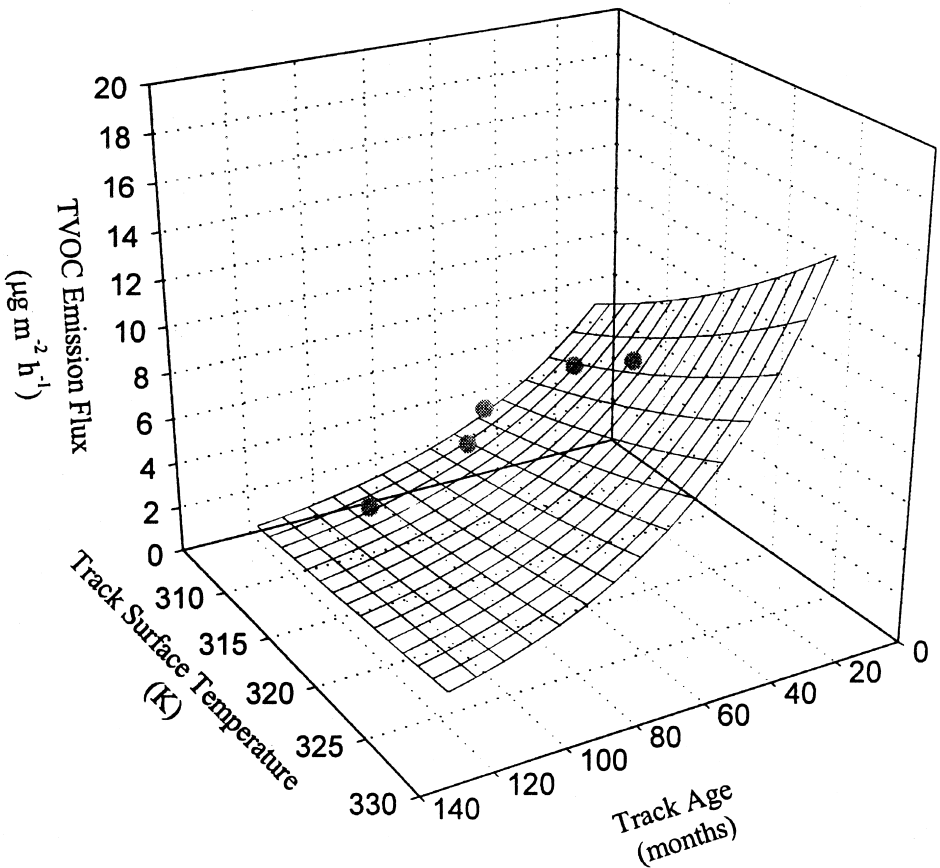

Fig. 4. Correlation of TVOC emission flux from Track PU-I with track age and track surface temperature.

and track surface temperature can be further examined using the Arrhenius equation [11,25–27]. The Arrhenius equation can be used to quantify the general dependence of the TVOC emission process on temperature:

$$\ln J = \frac{-E_a}{RT} + \text{const} \tag{5}$$

where E_a is the apparent activation energy of TVOC emission, T is the track surface temperature (K) and R is the gas constant (1.9872 cal K^{-1} mol^{-1}).
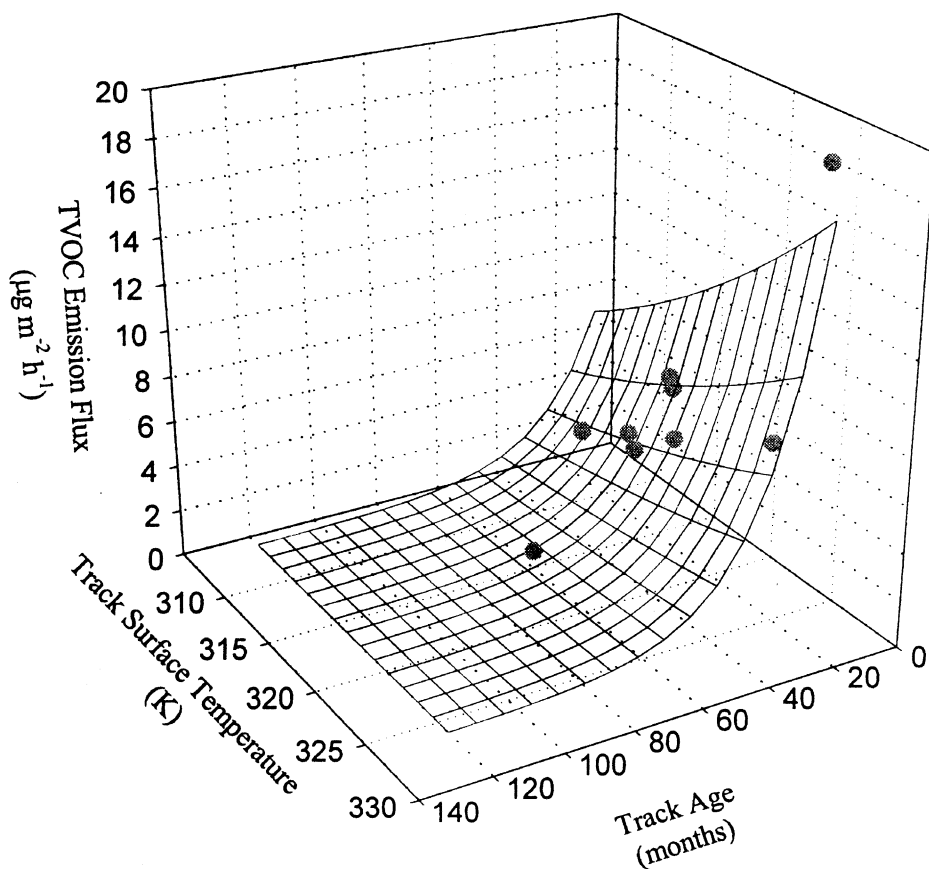
Track PU-II

Fig. 5. Correlation of TVOC emission flux from Track PU-II with track age and track surface temperature.

According to the Arrhenius equation $\ln J$ varies linearly with $1/T$, it is therefore logical to add the track-surface temperature as an additional term, thus giving Eq. (6):

$$\ln J = a_0 + a_1(t) + a_2\left(\frac{1}{T}\right) \tag{6}$$

where a_0, a_1 and a_2 are coefficients to be determined by curve fitting.

A multiple regression analysis applied to these data obtained in field study gave the results shown in Table 7 and Figs. 4–6 for Eq. (6).
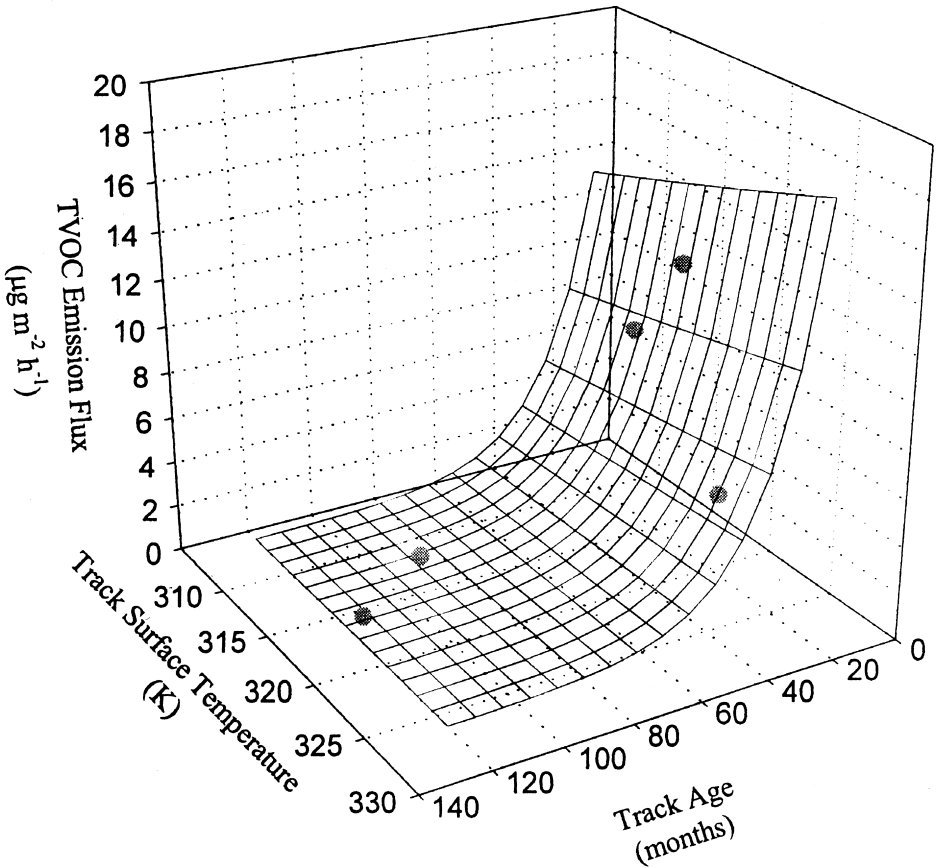
Track SR

Fig. 6. Correlation of TVOC emission flux from Track SR with track age and track surface temperature.

This analysis again shows the predominant effect of track age [t-test values: 3.18 (PU-I), 2.02 (PU-II) and 6.54 (SR)], while incorporating track surface temperature gave slight improvements in some of the correlations [t-test values: 1.15 (PU-I), 1.17 (PU-II) and 0.85 (SR)]. In other words, for tracks older than 2 years, the TVOC emission fluxes were more strongly affected by their age than by their surface temperature.

Also, the estimated initial TVOCs emission fluxes for Track PU-I, PU-II and SR, under general conditions ($t = 0$ month, $T = 313.15$ K), were 11.73, 17.22 and 26.75 $\mu g/m^2$ h, respectively. Because the initial TVOC emission fluxes, the track age
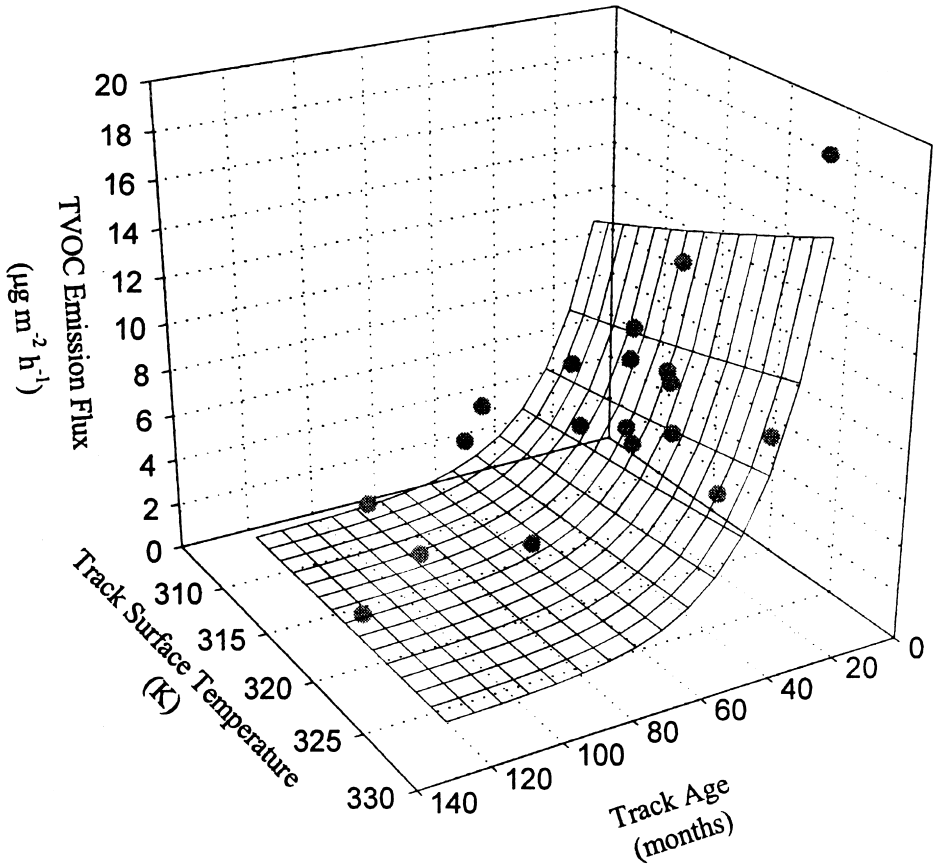

Fig. 7. Correlation of TVOC emission flux from each track with track age and track surface temperature.

Table 8
Time required to reach different reduction levels in TVOC emission flux

% Reduction	Time required (months)[a]			
	PU-I	PU-II	SR	All-Tracks
25	14	5	5	5
50	33	12	11	13
75	66	24	23	25
90	110	40	38	42

[a]A constant temperature of 313.15 K is assumed.

coefficients and the track surface temperature coefficients were about the same order of magnitude for all types of tracks, we also attempted to combine data from all types of tracks and obtained a single common correlation. As shown in Table 7 and Fig. 7, the results of multiple regression analysis also exhibit a fairly good correlation ($R_a^2 = 0.8137$). Clearly and similar to Figs. 4–6, the TVOCs emission flux decreased very rapidly in the early days after track installation. This supports our earlier hypothesis.

According to the correlation functions described in Table 7, the time needed to reach a certain reduction of TVOCs emission flux for each kind of track may be calculated, and its results were listed in Table 8. The results showed that releasing of VOCs from Track SR was much faster than the other two tracks. For Track SR, it took, respectively, about 5, 11, 23 and 38 months for TVOCs emission flux to reduce by 25%, 50%, 75% and 90%. However, for Track PU-I, the required time to reach the same reduction levels nearly tripled. This means that the more gas permeable a track is, the faster the VOCs are released. These results agreed with our understandings obtained in the preliminary study of tracks prior to full-scale field samplings (Table 1).

Table 9
VOCs concentrations at breathing height ($\mu g\ m^{-3}$)

Compounds	Tracks						Shah et al.[c]	
	PU-I[a]	PU-I[b]	PU-II[a]	PU-II[b]	SR[a]	SR[b]	Rural	Sub-urban
Benzene	1.13	1.22		0.86			1.48	5.73
Toluene + octane	1.22	1.17	1.31	0.13*	0.27*	0.65	1.31	0.73
Hexanal			0.77				–	–
Nonane + ethylbenzene	0.04*	0.14*	0.31*				–	–
Xylenes + styrene	0.88*	1.40	1.12	0.26*	0.12*	0.55*	–	–
Benzene, 1,2,3-trimethyl		2.02	0.68*				–	–
Undecane		0.43*					–	–
TVOCs	3.27	6.38	4.19	1.25	0.39	1.20	–	–

[a]Above the track.
[b]Far away from the track (background).
[c]Data obtained from Shah's [32] study.
*Below the MDL.
–No data provided.

3.5. VOCs concentration at breathing height

In this part, six samples were taken, including three samples from above the track and three samples far from the track (background). Table 9 lists the VOC concentrations at breathing height for all samples and the daily VOC median concentrations, which were obtained from rural and suburban sites in Shah's [32] study. Obviously, our measurements, those discussed above, differ from Shah's only slightly. In other words, the impact on ambient environment and the health hazard to school children posed by the VOCs released from older athletic tracks was not as serious as many people thought.

4. Conclusions

(1) The actual VOC emission behavior for each individual athletic track may vary considerably. A great many factors, including track age, additives and solvents used, construction and installation methods, wind speed, humidity and precipitation as rain or snow, time in the day and surface temperature at which the VOCs are sampled, may all affect the emission rate of volatile compounds. This study has shown that the emission rate depends on track age and temperature.

(2) The amount of VOCs contributed by older athletic tracks (> 2 years) to the ambient environment was very low. Furthermore, the actual concentrations of VOCs measured above the track at the breathing height were far below the threshold limit values regulated for ambient or industrial exposures in Taiwan. It is therefore believed that tracks older than two years will not cause any significant increase in the risk of serious health problems.

(3) For Tracks PU-II and SR, which had better gas permeability, their VOC emission flux decayed much faster. On the good side, these tracks are safer to use after being installed for a period of years. On the bad side, these tracks may emit larger amount of VOCs during the early weeks or months of use, and hence pose a more serious threat to the public.

(4) Even though some more reactive and more volatile noxious compounds (e.g. isocyanates, formaldehydes) [1,19,33] are assumed not to be found in older athletic tracks, they still could be and probably are emitted by tracks during track installation and the initial days of use.

(5) Hexanal is (see Table 4) the principal compound found in all tracks studied. We hope that in future studies, of tracks similar to ours, hexanal can be considered as an index compound. That is, by solely measuring hexanal we may be able to (1) understand the parameters affecting track emission and (2) understand the extent of reduction of all other VOCs and the TVOCs.

(6) A simple mathematical model involving track age and track surface temperature as parameters has been developed for estimating the TVOC emission fluxes from athletic tracks.

(7) Ideally, continuous investigation of the same sets of new tracks, starting from the day they are built, would be very helpful. Regretfully, due to public suspicion of potential health hazard posed by the VOCs emissions from synthetic athletic tracks, no

new synthetic tracks were build in southern Taiwan during the past 2 years. More informative and much more conclusive data could have been obtained had newer tracks been available.

Acknowledgements

References

[1] G. Oertel, Polyurethane Handbook, Hanser Publishing, 1994.
[2] K.Y. Lai, Fundamentals and Applications of Polyurethane, Fu-Han Publishing, Taiwan, 1993.
[3] Taipei City Government, A test report on PU track materials used in schools in Taipei, 1996.
[4] B.M. Eklund, M.R. Kienbusch, D. Ranum, Radian, 1984.
[5] W.D. Balfour, C.E. Schimdt, B.M. Eklund, J. Hazard. Mater. 14 (1987) 135.
[6] A.R. Gholson, J.R. Albritton, R.K.M. Jayanty, J.E. Knoll, M.R. Midgett, Environ. Sci. Technol. 25 (1991) 519.
[7] D.R. Reinhart, D.C. Cooper, J. Air Waste Manage. Assoc. 42 (1992) 1067.
[8] D.E. Rolston, in: Methods of Soil Analysis: Part I. Physical and Mineralogical Methods, American Society of Agronomy, Madison, WI, 1986.
[9] M.L. Wesely, D.H. Lenschow, O.T. Denmead, in: Global Tropospheric Chemistry: Chemical Fluxes in the Global Atmosphere, National Center for Atmospheric Research, Boulder, CO, 1989.
[10] F. Gao, S.R. Yates, M.V. Yates, J. Gan, F.F. Ernst, Environ. Sci. Technol. 31 (1997) 148.
[11] A. Carpi, S.E. Lindberg, Environ. Sci. Technol. 31 (1997) 2085.
[12] C.W. Thornthwaite, B. Holzman, Mon. Weather Rev. 67 (1939) 4.
[13] L.H. Parmele, E.R. Lemon, A.W. Taylor, Water Air Soil Pollut. 1 (1972) 433.
[14] I.J. Tinsley, Chemical Concepts in Pollutant Behavior, Chapter 4, Wiley, New York, 1979.
[15] W.A. Jury, W.F. Spencer, W.J. Farmer, J. Environ. Qual. 13 (1984) 573.
[16] J.E. Woodrow, J.N. Seiber, L.W. Baker, J. Environ. Sci. Technol. 31 (1997) 523.
[17] B.R. Hillery, I. Basu, C.W. Sweet, R.A. Hites, Environ. Sci. Technol. 31 (1997) 1811.
[18] K.T. Valsaraj, R. Ravikrishna, B. Choy, D.D. Reible, L.J. Thibodeaux, C.B. Price, S. Yost, J.M. Brannon, T.E. Myers, Environ. Sci. Technol. 33 (1999) 142.
[19] A.T. Hodgson, J.D. Wooley, J.M. Daisey, J. Air Waste Manage. Assoc. 43 (1993) 316.
[20] W.A. Jury, R. Grover, W.F. Spencer, W.J. Farmer, Soil Sci. Soc. Am. J. 44 (1980) 445.
[21] W.A. Jury, W.F. Spencer, W.J. Farmer, J. Environ. Qual. 12 (1983) 558.
[22] W.A. Jury, W.F. Spencer, W.J. Farmer, J. Environ. Qual. 13 (1984) 567.
[23] W.A. Jury, W.F. Spencer, W.J. Farmer, J. Environ. Qual. 13 (1984) 580.
[24] D. Mackay, Multimedia Environmental Models: The Fugacity Approach, Lewis Publishers, Chelsea, MI, 1991.
[25] Z.F. Xiao, J. Munthe, W.H. Schroeder, O. Lindqvist, Tellus 43B (3) (1991) 267.
[26] A. Carpi, S.E. Lindberg, Atmos. Environ. 32 (1998) 873.
[27] S.M. Siegel, B.Z. Siegel, Water, Air, Soil Pollut. 40 (1988) 443.
[28] B. Eklund, J. Air Waste Manage. Assoc. 42 (1992) 1583.
[29] M.D. Bortoli, E. Ghezzi, H. Knöppel, H. Vissers, Environ. Sci. Technol. 33 (1999) 1760.
[30] J.C. Ryden, L.J. Lund, D.D. Focht, Soil Sci. Am. J. 42 (1978) 731.
[31] W.A. McClenny, R.W. Shaw, R.E. Baumgardner, R. Paur, A. Coleman, R.S. Braman, J.M. Ammons, EPA-600/2-79-004, January 1979.
[32] J.J. Shah, H.B. Singh, Environ. Sci. Technol. 22 (1988) 1381.
[33] T.J. Kelly, D.L. Smith, J. Satola, Environ. Sci. Technol. 33 (1999) 81.