Bull. Environ. Contam. Toxicol. (2004) 72:255–260
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DOI: 10.1007/s00128-003-8686-3

Environmental
Contamination
and Toxicology

Aromatic Volatile Organic Compounds Emissions in a Tire Recapping Unit

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Received: 26 June 2002/Accepted: 19 October 2003

Samplings were performed in order to characterize the volatile organic compounds emissions in a tire-recapping unit. This unit is located in the city of Itatiaia, approximately 170 km to the south of the city of Rio de Janeiro. The study was performed in the outside area of the unit, in the direction of the predominant winds. The places and number of sampling points were determined through a plume dispersion calculation with the SCREEN software from US-EPA. The sampling was conducted with two groups of cartridges, one of active charcoal and the other of XAD-2, using six portable battery-operated personal air pumps. The compounds were identified and quantified by gas chromatography using a flame ionization detector. Some compounds were also identified by gas chromatography coupled with mass spectrometer.

Six compounds were identified: toluene, styrene, 4-chloro toluene, 4-chloro styrene, benzo (a) anthracene and chrysene. Concentrations of toluene and styrene were bellow the limits recommended by NIOSH. For the other compounds there are not well defined toxicological limits.

MATERIALS AND METHODS

In this work, the standard BTEX and PAH solutions, as well as sampling cartridges (active coconut charcoal, 100mg and Supelpak 20U, 100mg) from Supelco were used. Methanol (Omnisolv) was purchased from Merck.

Samples were collected using six portable battery-operated air pumps (SKC model PCXR) calibrated with digital flow calibrator (SKC Accuflow). Samples were collected using an active charcoal cartridge coupled with an XAD2 cartridge.

After sampling, the cartridges were eluted with methanol, up to the volume of 10mL, in a volumetric flask, for further analyses. Some compounds were also identified by gas chromatography coupled with mass spectrometer.

Identification and quantification of the compounds were performed by GC-FID, using a Perkin Elmer Autosystem gas chromatograph, with a split injector (1:75) at 250°C. The injection volume was 5µL. Helium was employed as carrier gas, at a pressure of 30 bar (1.3 mL/min). A Quadrex capillary column (100% methyl silicone, 50 m, 0.25 µm, 0.25 mm) was employed with temperature programming from 70°C to 100°C at 5°C/min, 100°C to 200°C at 20°C/min and 200°C to 320°C at 10°C/min. Detector was kept at 250°C.

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Our main goal was to evaluate the occupational exposure levels of workers at the outdoors circulation area of the tire-recapping unit, located at the city of Itatiaia, south of Rio de Janeiro, Brazil. This unit is equipped with one chimney and two exhausters, for removing of organic compounds associated with particulate matter and volatile organic compounds used in the recapping process, respectively. These exhausters and chimney are considered the most dangerous source of pollutants at this unit.

A preliminary sampling was performed in order to evaluate the breakthrough limit of each sampling cartridge and the optimum flow rate and sampling time. These conditions depend on the total pollutant concentrations and also, the detection limits of the analytical method employed for identification and quantification. Six preliminary samplings were tested using flow rates of 500, 1000 and 1500 mL/min for 30, 60 and 90 minutes. The best performance was achieved with a 1000mL/min flow rate for 60 minutes.

The sampling locations were chosen with a computational code SCREEN, from US-EPA. This software simulates the plume dispersion from stationary sources, showing how the pollutants are dispersed and which places are to be considered as the most dangerous for workers. The initial conditions and input values are: the height of the stack sources (from the ground), the gas flow, the estimated concentration for each pollutant (estimated from a sampling at the exit of the chimney), the gas flow temperature, the ambient temperature, the speed of the wind and the atmosphere classification. The last parameter is related to Pasquill (1974) standards, further modified by Dobbins (1979), and estimated as class B. Solar flux was considered to be moderate to strong.

The output consists of the concentration profile of the pollutants in the downwind direction. These data were used to estimate the number and best location of the sampling points.

Sampling positions were chosen to cover the areas indicated by the plume dispersion calculations as well as the usual circulation area of the workers. Two other samples were collected in front of the exhausters and at the exit of the chimney. These two other sample points were chosen to: (1) characterize these sources; (2) determine the compounds emitted by the unit and (3) exclude species emitted by other sources. Finally, a total of eighteen samples were collected during winter, on July 6, 2001, in the locations described by Figure 1. Samples 1 to 9, 12 and 16 were collected in the morning, while the wind was at northwest direction and the remaining, in the afternoon, while the wind was at east direction.

RESULTS AND DISCUSSION

In all samples, the most abundant compounds were aromatic hydrocarbons: toluene, styrene, 4-chloro toluene, 4-chloro styrene, benzo (a) anthracene and chrysene. Two other compounds were also identified but they were not detected in the samples collected at the chimney and at the exhaust. Other anthropogenic or natural sources may emit them. The measured compounds are listed in Table 1. Average values were obtained using the data for points 1 to 18.

The experimental results are in agreement with the profile concentration obtained in the direction of the predominant wind. Calculated results were obtained using the SCREEN

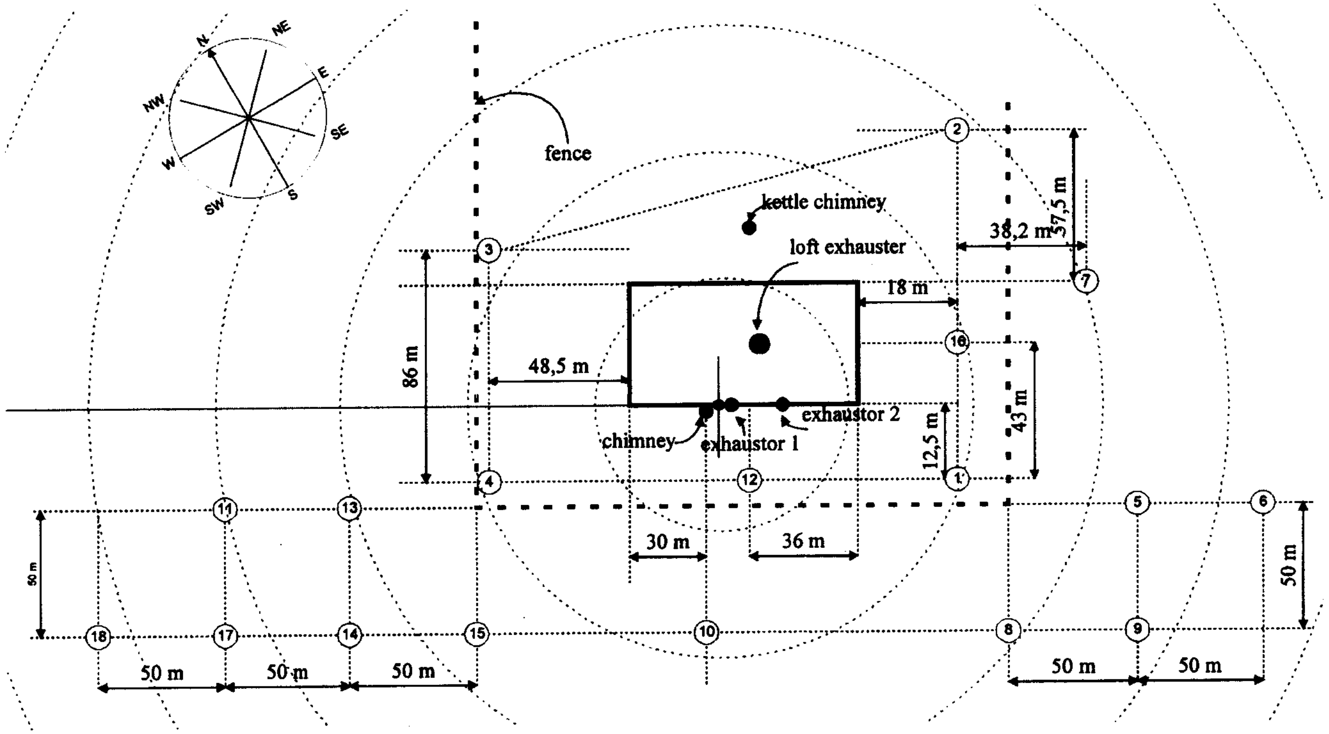

Figure 1. Location of the sampling points.

Table 1. Average concentration at each sampling point.

Sample Number	Sampled Volume (L)	toluene (mg/m^3)	styrene (µg/m^3)	4-chloro toluene (µg/m^3)	4-chloro styrene (µg/m^3)	benzo (a) anthracene (µg/m^3)	chrysene (µg/m^3)
1	59.3	12	8		9		
2	58.8	7	43			60	57
3	61.6	12	96	33	11	43	58
4	54.7	12	77			43	56
5	59.3		22				34
6	59.4	8	58	29		26	25
7	55.8	12	90	45	10	45	47
8	54.7	11	19			16	19
9	61.6	11	31		8		15
10	58.8	13	80	33	9	28	55
11	54.7	13	69	31	12	40	41
12	59.4	9	11				19
13	55.8	15	35		21	14	20
14	61.6	13	69	39	14	30	41
15	58.8	13	27				
16	55.8	10	23				17
17	59.3	15	38	23	14	27	32
18	59.4	12	48		13	23	21
Average	55.2	11.1	44.3	7.6	9.0	16.7	17.5
Exhauster	9.1	110	1185	735	116	667	702
Chimney	9.1	66	468	273	53	243	236

n=18

package, as described previously. The observed deviations may be due to the variations in wind speed and direction. These data show that SCREEN code was successful in calculating the plume dispersion in order to choose the sampling points. Both the grid spacing and the position of sampling points were determined on the basis of SCREEN's results. Variations in wind speed during the sampling period were not taken into account and may be responsible for the dispersion of the results. Maximum calculated values are in good agreement with experimental results.

Toluene was the major pollutant. It was detected in seventeen samples with an average value of 11.1 mg/m^3. This average value is lower than the NIOSH recommended limit of 375 mg/m^3 (TWA) and 560 mg/m^3 (ST). For styrene, the average value of 44.3 µg/m^3 is also lower than the NIOSH limit (215 mg/m^3 TWA and 425 mg/m^3 ST). The PAHs, benzo (a) anthracene and chrysene have not been legislated but NIOSH recommend concentration values as low as possible due to their carcinogenicity and mutagenicity.

Toluene is the main compound in the organic solvent mixture used to treat and clean the tires that will be recapped and is also used in styrene synthesis. Styrene is the main monomer of rubber and the chloro compounds are also used in tires manufacturing. The

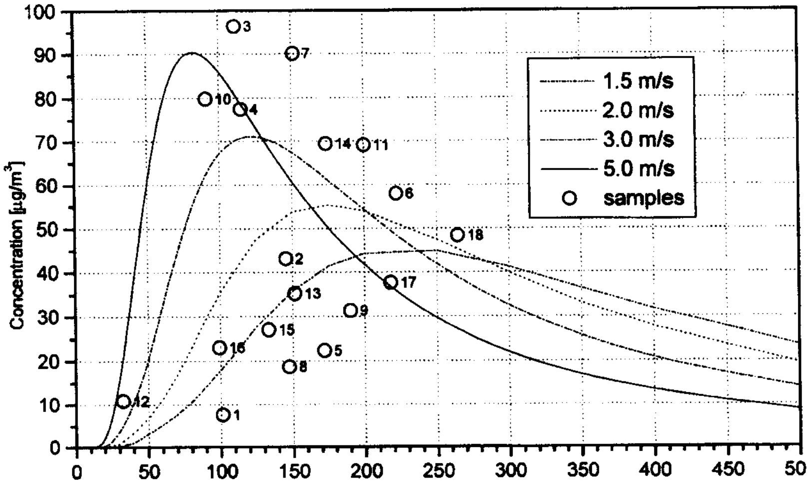

Figure 2. Experimental and calculated.concentrations for styrene. Simulated results were obtained using the SCREEN computational code and various wind speeds (from 1.5 to 5.0 m/s).

PAHs are formed during the incomplete combustion of organic matter and are always associated with particulate matter because of their high boiling points and vapor pressures.

The concentrations of the measured compounds are bellow the recommended values set by occupational agencies and do not represent a risk for workers' health. Nevertheless, some improvements may be suggested in order to minimize the exposure o workers. The installation of a cyclone, to improve the efficiency of the bag filters used to remove particulate matter in the chimney, and wet scrubbers or incinerators in the exhausters should be considered.

Acknowledgments. We thank Glauco Favilla Bauerfeldt for the revision of the manuscript and also thank CNPq for partial financial support.

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