DIOXINS IN SOOT COLLECTED FROM TUNNEL WALLS IN THE CITY OF RIO DE JANEIRO, BRAZIL

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Introduction

The City of Rio de Janeiro is situated in a mountainous landscape and hills dividing several urban areas. In order to guarantee quick translocation between these areas, various tunnels were constructed during the last century, summarizing about 60 tunnels. Passing by car through these tunnels, it can be observed that the walls are covered by a layer of black material, which obviously is originated from car exhaust and probably as well from tire and break abrasion. Vehicle exhaust is very well known as source for polychlorinated dibenzo-p-dioxins and dibenzofurans to the environment [1, 2, 3, 4] and consequently particulate matter deposited on tunnel walls should also be contaminated. Therefore, the objective of this study was to determine the dioxin concentrations in this material and to estimate the total amount deposited on the tunnel walls.

Materials and Methods

Tunnel description

In the year 2004, soot samples were taken from four tunnels located in different urban areas of Rio de Janeiro. Santa Barbara Tunnel, inaugurated in the year 1963, has a length of 1,357 m, a height of about 5.5 m and a frequency of about 110,000 cars/day. Rebouças Tunnel, inaugurated in the year 1967, has a length of 2,040 m, a height of 8.6 m and a frequency of 180,000 cars/day. Zuzu Angel Tunnel, inaugurated in the year 1973, has a length of 1,600 m, a height of about 5.9 m and a frequency of 110,000 cars/day. Convanca Tunnel, inaugurated in the year 1997, has a length of 2,187 m, a height of 6.3 m and a frequency of 85,000 cars/day. All tunnels, except Santa Barbara, have one tube for each direction. They are all equiped with an exhaust sytem using ventilators installed on the top of the tubes.

Sampling

Soot samples were collected from a marked area of one square meter, except Covanca Tunnel, where it was impossible to have a defined area due to the wall surface unevenness caused by the use of sprayed concrete to cover the crude rock. Wipe samples were taken in Santa Barbara Tunnel where the wall is covered with tiles. In the other cases, the soot was detached with a soft brush directly in the sampling container. In each tunnel one sample was taken in the middle and another in the last quarter of the tunnel.

Analysis

The applied analytical method was based on the principles of USEPA Method 1613. Samples were spiked with all 17 2,3,7,8-congeneres marked with ^{13}C and extracted with toluene during 24 hours in a Soxhlet apparatus. The cleanup procedure consisted of 4 single steps. The first step was a multi-layer column with silica, silica/sulfuric acid and silica/NaOH followed by a gel permeation column, a Florisil column and finally an activated carbon/silica column. The final extract was concentrated to 20 µl and spiked with the recovery standard. Instrumental analysis was conducted with an Agilent 5973 mass spectrometer coupled to an Agilent 6890N gas chromatograph. Separation was performed on a DB 5MS column (60 m, 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) with helium as carrier gas hold at 1,3 ml/min.

Besides the normal internal quality assessment procedures such as analysis of blank and reference samples, the laboratory was successful in participating in intercalibration studies.

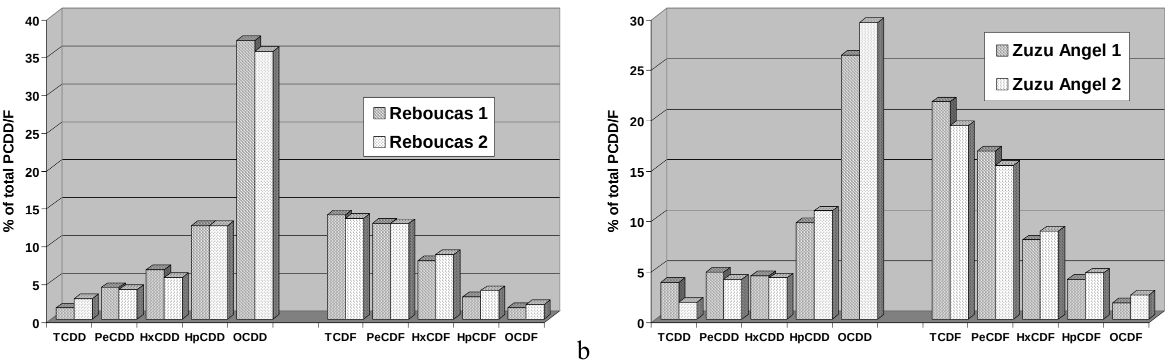
Results and Discussion
The results are presented in table 1.

Table 1: Dioxin concentrations found in soot samples from tunnel walls in Rio de Janeiro, Brazil.

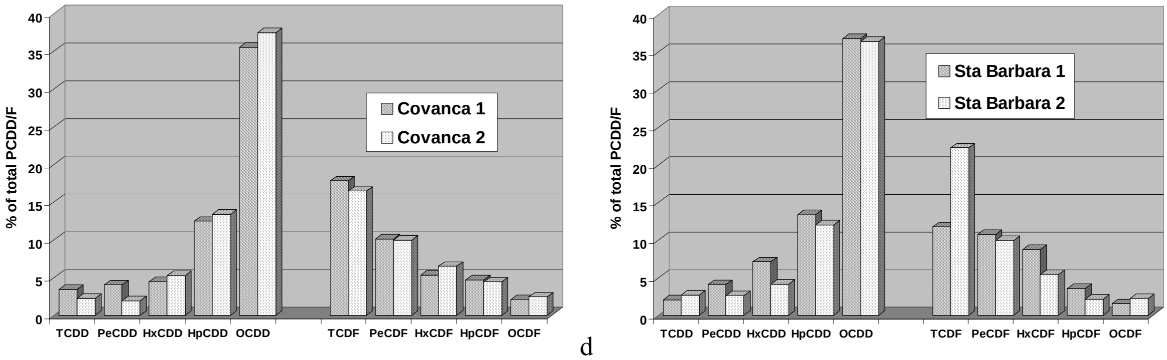
Tunnel*	Amount ng I-TEQ/kg	Amount ng I-TEQ/m^2	Median ng I-TEQ/kg	Median ng I-TEQ/m^2
Santa Barbara 1[a]	-	0.66	-	0.60
Santa Barbara 2[a]	-	0.55		
Rebouças 1[b]	116	27.1	108	25.8
Rebouças 2[b]	100	24.5		
Zuzu Angel 1[b]	66.5	4.47	60.5	4.06
Zuzu Angel 2[b]	54.4	3.65		
Covanca 1[c]	45.0	-	44.4	-
Covanca 2[c]	43.9	-		

* Sample point 1 = middle, Sample point 2 = last quarter
[a] wipe sampling, 1 m^2; [b] detached soot sampling, 1 m^2; [c] detached soot sampling, undefined area

The soot collected in the Rebouças Tunnel showed the highest concentration with the median of 108 ng I-TEQ/kg, followed by Zuzu Angel Tunnel with 60.5 ng I-TEQ/kg and Covanca Tunnel with 44.4 ng I-TEQ/kg. Since the samples from Santa Barbara Tunnel were wipe samples, concentration can be reported only in ng per square meter. Through different sampling procedures, direct relation between sampled area and weight of collected material was possible for Rebouças and Zuzu Angel. The transformed values of 25.8 and 4.06 ng I-TEQ/m^2, respectively, showed that the Santa Barbara Tunnel is the lowest contaminated tunnel with the median value of 0.60 ng I-TEQ/m^2 even if it is the oldest one. This could be explained by the fact reported by the tunnel operators. The tunnel was cleaned once in the 90's. More over the covering by tiles could have influence to the adsorption properties.
The homologue distribution patterns are shown in figure 1 a-d. Generally, they are very similar with dominant OCCD and PCDDs decreasing rapidly from OCDD to TCDDs, contrary to the PCDFs, where TCDFs demonstrate the highest amount decreasing slowly to OCDF. Main differences were observed in the amount of PCDFs relative to the OCDD. Especially the samples from Zuzu Angel Tunnel showed TCDFs almost as high as OCDD. In the other samples, the relative TCDFs amount is about the half of the OCDD. Inconsistence was recognized between the two samples collected from Santa Barbara Tunnel with high difference in the relative TCDFs amount. The sample 2, collected in the last quarter of the tunnel, had about the double of TCDFs compared to the sample collected in the middle. However, other authors reported similar distribution patterns in immission samples from road tunnels and motor exhaust samples [3,5,6].



a b
Figur 1: Homologue distribution patterns: (a) Rebouças Tunnel, (b) Zuzu Angel Tunnel



c d

Figur 1: Homologue distribution patterns: (c) Covanca Tunnel, (d) Santa Barbara Tunnel

The total PCDD/F amount stocked at the walls was estimated for the three tunnels with concentrations given in ng/m^2. Three approximations were considered for calculation. First, the concentration is distributed homogenously through the whole length of the tunnel, second, the tunnel shape correspond the half of regular cylinder and third, concentrations are equal in both tubes. Santa Barbara Tunnel showed the smallest amount with 0.014 mg I-TEQ followed by the Zuzu Angel Tunnel with 0.24 mg I-TEQ. The highest value of 2.84 mg I-TEQ was found in the Rebouças Tunnel. These results demonstrated that tunnel walls could be a small sink for PCDD/Fs originated from vehicle exhaust and tunnel operator should be aware of this fact due to, as already mentioned, possible cleaning processes, which can lead to exposure of working personal and contamination of other environmental compartments, mainly the water bodies.

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