PAHs emissions by Brazilian bitumens

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ABSTRACT

In the last few years, there has been a great focus with human health and improvement in workers' conditions. Within this context, it is necessary to study the impact caused by the highway construction in people's life quality. This paper aims to study PAH's (Polycyclic Aromatic Hydrocarbons) emission from different bitumens commercialized in Brazil (conventional, modified by polymer or rubber and natural asphalt). The bitumen's were submitted to conventional tests (brazilian specifications) and rheological (SUPERPAVE classification). The most usual application method is hot mixture. When heated, the asphalt releases volatile species and solid particles carried by gases which mixture is called bitumen emissions. Ian this fume there are organic substances (PAH`s), and some of which may be carcinogenic. Therefore, the fume emitted in the bitumens heating is harmful to health and should be considered, both from the environmental sustainability and the worker`s health point of view. PAH`s studies were done alongside with other studies about bitumens where the bitumen and the emission of some PAH`s were correlated, which will be measured through an experimental apparatus that generates and collects the bitumen fume. This equipament is nominated ECD (extraction and collection device). The fumes are collected and analyzed by LC-MS/MS (liquid chromatography mass spectrometry) to quantify the amount of emitted PAH`s. From the research, it will be possible to verify if bitumens with different behaviors at paving have, from the perspective of sustainability, different impacts to the environment and human health. These emissions, although low, have an impact not well known on health and environment.

Keywords: Asphalt, Environment, Fumes, Health Safety and Environment, Safety

1. INTRODUCTION

The road works comprise a broad spectrum of services involving engineering, diversity of materials, specialists and workers who are submitted to working spreading the asphalt. More than 90% of national roads are paved in asphalt coating (ABEDA, 2014). In Brazil, the main mode of movement of goods and people is by road. Because of the relevance of this kind of transportation, comes the need to conserve and expand the paved road network. During the execution phase in asphalt roads is common to use high temperatures to promote mixing and also application. In addition to the high energy consumption and the level of discomfort when working with heated material, there is the important issue of health at work when talking about inhalation of asphalt fumes, which contain low concentrations of PAHs (Polycyclic Aromatic Hydrocarbons). This emissions, although low, have an impact shown by IARC in 2013, where it is stated that this issue is important and indicates some values and considerations which so far are not considered standardization.

In general it is known that there are numerous substances harmful to health, among them there are the PAHs. PAHs are composed of more than 100 volatile chemicals, some of which may present risk of developing diseases like cancer. According to Baird (1999), generally hydrocarbons having Benzene properties are called aromatic, and in the presence of two or more fused benzene rings they become known as PAHs.

When products from the asphalt are subjected to high temperatures, they emit some hydrocarbons including PAHs in low concentrations, which some of them are suspected of being mutagenic and/or carcinogenic (NIOSH, 2000; RAVINDRA et al., 2008; YASSAA et al.,2001; FERNANDES et al., 2009).

Therefore, there is need for research and development of new methodologies for investigating bitumen fumes and specifications for the implementation of better roads and ensure the health and safety for workers during the execution process of highway work. Once the investments in road infrastructure have increased and labor regulations have become increasingly stringent for safety and health at work, the application of materials that are not harmful to human health is of paramount importance.

Within this context, this paper use a bitumen fume extraction technique to evaluate 12 binders sold in Brazil and invested in road works, featuring its emissions of PAHs in mixing and application temperatures.

2. BIBLIOGRAPHIC REVIEW

This bibliographic review is arranged in three parts: the first refers to occupational health, one of the motivations for this research. The second part deals with the study material, bitumen. The third part of the review is about PAHs. Finally, the fourth part is about existing methods for lab generation of bitumen fumes.

2.1. Occupational health

When bitumen is heated at high temperatures, occur bitumen emissions. Among the emissions highlights are bitumen fumes which contain, among other substances, PAHs. Thus, the workers that use the heated bitumen are exposed to bitumen fumes that contain PAHs.

Through a thermo graphic camera is possible to measure the temperatures of the asphalt in degrees Celsius. In a study conducted by GEPPASV (Group of Studies and Research in Paving and Road Safety of the Federal University of Santa Maria) in 2015, a thermographic camera was used to verify the application and mixing temperature of materials during the paving process. It made possible to observe the high temperatures that workers are exposed to. For this work Figure 1 was selected, which highlights the asphalt's thermal range and the high temperatures that it application has and which workers are exposed to.

Figure 1: Thermographic camera image picturing the handling of asphalt which temperature scale is in Celsius.

According to Lopes, 2008, the acute symptoms in pavers involve: eye irritation, irritation of mucous membranes of the upper respiratory tract (nose and throat), coughing, dyspnea, chemical asthma, bronchitis, headache, irritation, dryness and skin irritation, rashes, cracks and wounds.

In IARC Monograph 103, 2013, was made a review of possible diseases caused by exposure pavers to bitumen fumes and for cancer of the lung, cancer of the urinary bladder, cancer of the upper airway and upper digestive tract and an association between cancer at other sites (e.g. stomach, kidney, leukaemia and skin) and the result of the review were inconclusive. There is inadequate evidence in humans for the carcinogenicity of occupational exposures to bitumens and bitumen emissions during road paving. In studies of pavers, bitumen emissions, produced higher levels of mutagenic urine, increased DNA damage, and increased levels of sister-chromatid exchange, micronucleus formation and chromosomal aberrations in human lymphocytes compared with control populations. These positive genotoxic findings in pavers provided strong evidence for a genotoxic mechanism for a tumorigenic effect of exposures to bitumens and bitumen emissions in pavers (IARC, 2013).

2.2. Bitumen

Bitumen is a derivative residue from petroleum refining and contains a mixture of aliphatic hydrocarbons, paraffin, aromatic compounds containing carbon, hydrogen, oxygen and nitrogen, including, PAHs (GUIMARÃES, 2003). Bitumen is also called binder, and its production in Brazil began in 1956, at Presidente Bernardes Refinery in São Paulo. According to Roberts, 1991, bitumen can be found in solid, pasty and fluid state when diluted and heated. There are two basic classifications for bitumen: paving, object of this study, and industrial, where they fit oxidized asphalts which are used for waterproofing, for example.
The way the atoms form the asphalt binder is extremely complex and the proportion of these molecules formed by atoms and the way they interact affect the behavior of the material. Since this is a complex matrix, the asphalt binders are difficult to characterize because these characteristics also depend on where the bitumen is extracted. They are generally composed of 90 to 95% hydrocarbon and from 5 to 10% of heteroatoms such as oxygen, sulfur, nitrogen and metals such as nickel, iron and vanadium (Read; Whiteoak 2003).

2.2.1. Specification of bitumen

The trials performed to measure the physical properties of the bitumen have specific temperature and some also determine the loading time and speed. To characterize a particular asphalt as suitable for paving, most countries use simple measures of physical properties of bitumen, because of its ease of implementation in the work laboratories. The two major properties used are: a "hardness" measured by a standard needle penetration in bitumen sample, the resistance to flow, measured using the viscosity tests.
The Brazilian specification is according to the classification system of the Departamento Nacional de Infraestruturas de Transporte (DNIT - National Department of Transport and Infrastructure) standards. In Brazil, the conventional bitumen's are classified into: CAP 30/45, CAP 50/70, CAP 85/100 and CAP 150/200. They receive this nomenclature according to the results of the penetration study described in standard DNIT 155/2010-ME.
For a more complete spectrum of the characteristics of bitumen to be used in this work, other tests were performed, agreed by Brazilian standards beyond the penetration test, as the bitumen used are not only conventional above.
The other bitumen used in this work also follow the DNIT standards which are used for testing and material specifications. The standards for each type of bitumen are listed in Table 1.

Table 1: DNIT standard specifications for each type of bitumen.

Type of bitumen	Specification
CAP conventional	DNIT 095/2006 - EM
CAP modified by elastomeric polymer	DNIT 129/2011- EM
CAP modified by waste tire rubber powder	DNIT 111/2009 - EM
CAP modified by natural bitumen	DNIT 168/2013-EM

2.3. Polycyclic aromatic hydrocarbons (PAHs)

Emissions from hot bitumen are composed of fumes from hot bitumen and gases. The fumes from hot bitumen may contain irritating agents and small amounts of polycyclic aromatic compounds. Among these compounds issued, one part is formed by PAHs. (BINET *et al*, 2002, BONNET et al, 2000 KRIECH *et al*, 1999)
Due to the high variability of the samples of bitumen and its high complexity, to define the exact chemical composition of the generated fumes is not a feasible task, but can generally highlight the presence of hydrocarbons and methane, sulfur dioxide, carbon monoxide, dioxide nitrogen, hydrogen sulfide and aromatic solvents such as benzene, toluene and xylene. However, in the occupational health point of view, the most important components due to its carcinogenic action are the PAHs (GODOI, 2011, FERNANDES et al, 2007, BOCZKAJ et al, 2014).
As mentioned, the asphalt binders release fumes which have PAHs. The PAHs belong to a class of complex chemical compounds whose structure is in the form of linked benzene rings, and is widely distributed in the atmosphere. However, some PAHs have already been considered to have carcinogenic and / or mutagenic potential.
The United States Environmental Protection Agency (USEPA) ranked sixteen PAHs as priority in relation to health and the environment: Naphthalene (Na), Acenaphthalene (Ac), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Ph), Anthracene (An), Pyrene (Py), Chrysene (Ch), Fluoranthene (FL), Benzo [a] anthracene (BaA), Benzo [b] fluoranthene

(BbF), Benzo [k] fluoranthene (BKF), Benzo [a] pyrene (BaP) Dibenzo [a, h] anthracene (DA), Benzo [g, h, i] perylene (BPE) and indeno [1,2,3-c, d] pyrene (IP).
The composition of bitumen fumes is quite complex and beyond the PAHs there are several other substances potentially harmful to health, (e.g. asphaltenes, straight and branched aliphatic hydrocarbons, naphthene aromatics and resins. WHO, 1998).
The PAHs have received more attention because of the possible long-term damage caused by chronic health hazard.
According to Ferraz, 2015, PAHs may exist in more than one hundred combinations, however countries adopt different lists of priority PAHs that may be a group between 16 and 28 different compounds. Brazil usually adopts in research EPA's (Environmental Protection Agency) list, used in the US and presented in Table 6, where 14 PAHs are considered priority for this job.
Even though there is scientific evidence and it is possible to determine the carcinogenic potential of bitumen fumes in humans as proposed by IARC in 2013, yet there are no norms that regulate the amount of each PAH emissions. The lack of consolidated information should not impede actions to minimize the preventive measures but to seek more data to fill gaps in knowledge on the subject.

2.4. Existing methods for lab generation of bitumen fumes

Besides the ECD (Extraction and Collection Device) which was the equipment used in this study, there are other PAHs extraction devices in the literature. Among the numerous devices developed since then, in 2002, BINET et al proposed the fumes generator design that allows adjustments in the fumes emanation area with the use of interchangeable components for fumes with PAHs content proportional to the concentration of fumes in terms of total particulate material. PREISS et al, Part 1, POHLMANN et al, 2006, collected fumes directly from bitumen storage tanks. The collected bitumen fumes were subsequently regenerated for inhalation tests in rats and according to the authors, considering that the condensate regenerated fumes are comparable to the material collected in personal samplers used in the workplace, so the generated laboratory atmosphere can also be compared with the atmosphere of the workplace.

3. MATERIALS AND METHODS

For the experiments on ECD (Extraction and Collection Device) it was necessary to develop the methodology, from sample preparation to filter the fumes adsorbed to analysis in LC-MS (Liquid Chromatography Mass Spectrometry).

3.1. Materials

This work will analyze twelve bitumen samples produced and used in Brazil. Conventional bitumen samples are, in this case, CAP 30/45 and CAP 50/70. All bitumen samples, both conventional and modified, used in this work are listed below with their main characteristics:
- CAP 50/70: It is a bitumen considered medium;
- CAP 30/45 (provider A and B): It is a bitumen considered hard;
- FLEXPAVE 60/85: It is modified by elastomeric polymer (SBS);
- ECOFLEX B: It is modified by waste tire rubber powder (rubber bitumen);
- HARD CAP: Industrial secret. This bitumen has the rheometric characteristics differentiated especially for large loads;
- CAP Borracha: It is modified by waste tire rubber powder (rubber bitumen);
- CAP TLA Modificado: 25% natural bitumen + 75% modified bitumen;
- CAP TLA AM: Modified with national bitumen and natural bitumen coming from the asphalt lake (from Trinidad and Tobago);
- Stylink: It is modified by an addition of polymer.

Besides the binders mentioned above, highly modified asphalt (HIMA) are studied:
- HIMA I: High concentration of elastomeric polymer (SBS); HIMA II: High concentration of elastomeric polymer (SBS).

The twelve binders sampled for this work are the most commonly used in Brazilian paving.
Hereafter, will be present the results of the test to the Brazilian ratings and *Superior Performance Asphalt Pavements* (SUPERPAVE) which were used to characterize the materials in the laboratory before making the extraction of PAHs. It is very important that the material is known and properly specified to make analyzes of asphalt emissions.
- Brazilian specification:

The bitumen samples in the study were subjected to characterization tests by GEPPASV group. The results of the aforementioned tests are shown in Table 2 and are relevant to demonstrate the actual characteristics of the bitumen sampled for subsequent tests in ECD.
Results for Brookfield viscosity trials for the twelve binders under study are exposed in desirable temperature obtained by calculation for mixing and application, because the aim of this study is to verify the emissions of bitumen at different temperatures. In addition to viscosity results are presented the results of elastic return trials, softening, penetration, flash and fire point and density in Table 2.
- SUPERPAVE specification:

As a result of tests regulated by SUPERPAVE's standards, temperatures and traffic which are the suitable for bitumen application are obtained. This classification method achieves better results for application of materials in accordance with the place where the road is to be built. Table 3 summarizes the results from trials with bitumen of this study using the SUPERPAVE classification.

Table 2: Trials results of viscosity, elastic return, softening, penetration, flash and fire point and density for bitumen in study.

Bitumen	Mix temp.	Application temperature	Elastic Return (%)	Ring and ball (ºC)	Penet. (0,1 mm)	Flash Point (ºC)	Fire Point (ºC)	Density (g/cm³)
Hard CAP	166 to 172	156 to 160	17,6	66,5	36,8	238	289	-
50/70	148 to 154	137 to 142	10,8	51,9	59,6	266	292	1,0175
30/45 B	159 to 164	150 to 154	8,9	55,75	42,6	328	359	-
30/45 A	165 to 170	156 to 160	17,1	62,85	46,8	267	299	-
TLA Modif.	164 to 170	154 to 158	12,6	60,8	38,2	275	340	1,082
Flexpave	-	-	89,2	82,3	55,2	275	330	-
Stylink	172 to 179	160 to 165	23,8	69,4	72,4	278	326	1,0365
HIMA II	-	95,3	86,5	53,9	318	350	1	1,006
HIMA I	-	-	-	41,6	-	-	-	-
TLA AM	181 to 187	170 to 175	60,6	69,65	22,7	298	344	1,1335
Ecoflex B	204 to 214	187 to 194	69,2	63,35	49,8	253	294	-
Borracha	-	-	65,8	62,85	71,6	310	320	-

Table 3: Results of bitumen samples under study obtained through the trials of SUPERPAVE methodology at COPPE / UFRJ.

Bitumen	PG	Traffic
Hard Cap	82-22	Extremely heavy traffic (E)
50/70	58-16	Heavy traffic (H)
30/45 B	82-16	Extremely heavy traffic (E)
30/45 A	70-22	Heavy traffic (H)
TLA Modificado	76-10	Very heavy traffic (V)
Flexpave (60/85)	82-22	Extremely heavy traffic (E)
Stylink (76/22)	70-28	Very heavy traffic (V)
HIMA II	76-28	Extremely heavy traffic (E)
HIMA I	82-22	Extremely heavy traffic (E)
TLA AM	70-22	Standart traffic (S)
Ecoflex B	82-28	Extremely heavy traffic (E)
Borracha	76-28	Heavy traffic (H)

3.1.1. Mix and application temperatures

For this study, there was the need to choose temperatures to simulate mixing and application of the asphalt when it comes to fumes extraction. The mixing temperature and application are the ones which workers are more exposed to bitumen.
To do this, they were taken from the supplier's specifications temperatures suitable for mixing and applying the asphalt concrete. It is noted that the temperatures in Table 4, which were reported by the supplier, resemble the temperatures in Table 2, where temperatures were obtained by the Brookfield test in GEPPASV laboratory.
In highway works it can be noted that the temperatures indicated by the bitumen suppliers are actually used, as occurs in this temperature range the highest yields using the material.
To start the test, the sample must be in a solid state for better handling. First the sample is weighed and fractionated according to the ECD capacity (approximately 100g).
Table 4 summarizes the temperatures indicated by suppliers for mixing and application, as well as mass used in each sample.

Table 4: Mixing and compaction temperatures of bitumen informed by suppliers and temperatures used in ECD during the trials.

Bitumen	Mass used (g)	Mix temperature (°C)		Application temperature (°C)	
		Informed	Used	Informed	Used
Hard CAP	115,3	-	168	-	158
50/70	110,3	150 to 155	152,5	Above 135	135
30/45 B	108,4	151 to 157	154	141 to 147	144
30/45 A	97,5	155 to 160	157,5	Above 140	140
TLA Modificado	120,1	155 to 161	158	146 to 152	149
Flexpave 60/85	95,4	160 to 165	162,5	Above 145	145

Stylink 76/22	132	160 to 166	163	141 to 147	144
HIMA II	114,5	171 to 175	172,5	161 to 165	162,5
HIMA I	113,4	170 to 175	173	160 to 165	163
TLA AM	199,3	161 to 167	174	146 to 152	149
Ecoflex	133,3	170 to 180	175	Above 150	150
Borracha	100,2	180 to 185	182,5	160 to 165	162,5

3.2. Method of extraction and collection PAHs using the Extraction and Collection Device

For removal of PAHs from bitumen, heating is required. When heated to high temperatures, above temperatures of flash point, the binder can catch fire and the experiment become unsafe. To avoid this problem, the equipment must operate at temperatures below the sample's flash point temperature and involve the material being kept under inert atmosphere (no oxygen). Furthermore, to capture fumes the system must be airtight to avoid PAHs dissipation.
This work uses the ECD (Extraction and Collection Device) developed by Ferraz in his doctoral thesis at the Federal University of Santa Maria in 2015, which is able to generate and collect fumes produced by heating bitumen samples. This device is suitable for use in the laboratory bench and the generation of fumes takes place through heating of the bitumen in a closed system, with controlled temperature in non-oxidizing atmosphere using heated argon as carrier gas. The extraction of the fumes are made from small masses of bitumen. The developed system was applied in generating and collecting fumes of the main bitumen sold in Brazil. The collected fumes were analyzed for concentrations of some PAHs whose monitoring is recommended by the World Health Organization because of its carcinogenic potential. The ECD can be operated in a wide temperature range, covering all the usual asphalt application temperatures without significant loss of analytes and with no risk of ignition under this inert atmosphere. The device can operate with different solvents in contact with the bituminous mass and also without the presence of these solvents, by direct heating of the sample.
The ECD allows the collection of the fumes either directly in liquid phase (absorbents solutions) or in solid phase (solid adsorbents). In the analysis of the collected fumes in the ECD were found 14 of the 16 priority PAHs by the USEPA:
Naphthalene (Na), Acenaphthalene (Ac), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Ph), Anthracene (An), Pyrene (Py), Fluoranthene (FL), Benzo [b] fluoranthene (BbF), Benzo [k] fluoranthene (BKF), Benzo [a] pyrene (BaP), Dibenzo [a, h] anthracene (DA), Benzo [g, h, i] perylene (BPE) and indeno [1,2,3-cd] pyrene (IP).
The ECD works as follows: A thermal resistance with temperature control heats the massive piece made of aluminum in conical shape. This piece of aluminum is in an environment where the temperature is maintained through rock wool heat insulating material. Bitumen is disposed within the cone and the ECD is closed by a stainless steel lid with the exit for fumes. The cone is heated in an environment controlled by thermometers and inert atmosphere due to the presence of argon gas (Ar). The gas is coming from a cylinder (with flow regulators), and before contact with the bitumen is heated through the serpentine around the heated piece of aluminum as shown in Figure 2. The injection of argon and heating is extremely important, because this way the bitumen does not go into combustion because of its inert site and doesn't cool. The heated bitumen releases the fumes which come out from the preferred path for the traps, which is the output at the top of the lid. Traps containing adsorbent liquid (acetonitrile) are immersed in ethylene glycol, a substance that cools the samples contained in traps. The device extraction and collection was outlined in Figure 2.

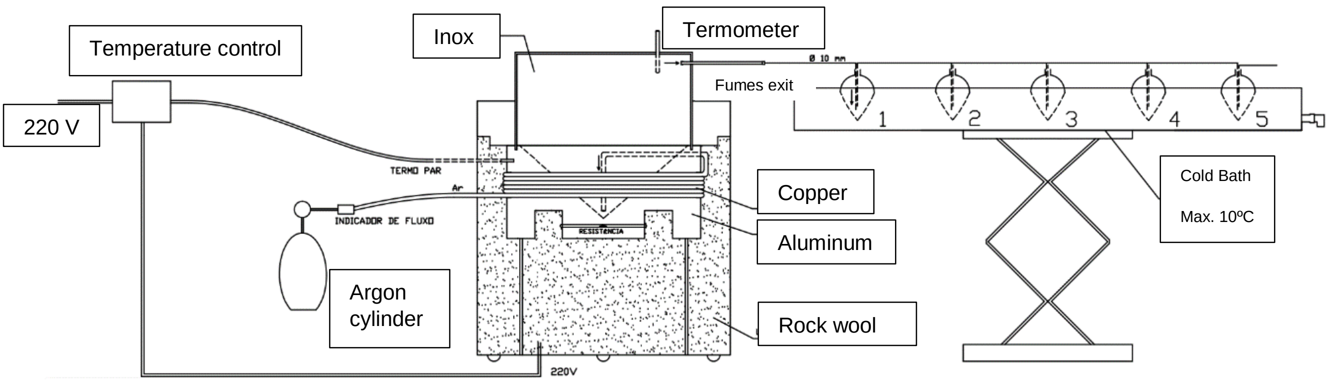

Figure 2: Schematic of operation and parts of ECD. Font: Ferraz, 2015.

The ECD is an equipment which consists of heating the bitumen in solid block of aluminum that have a conical shape with pressure and temperature control. This environment surrounding the bitumen consists of Argon gas that is heated to the same temperature as the bitumen, preventing the mass to cool (passed along the heating block of aluminum through the copper coils). There is a thermometer attached for measuring the temperature of the bitumen while heated.
As mentioned above, when the bitumen is heated it releases fumes which contain PAHs. This fumes are picked up by a glass trap system containing a solvent (acetonitrile), which adsorbs fumes. This adsorbed material is treated to become as translucent as possible and with the least number of species of PAHs which are not necessary to detect. The equipment in use can be seen in Figure 3. It is observed that the glass traps are in a PVC tube containing ethylene glycol to keep the

low temperature. To start the test, the sample must be in a solid state for better handling. First the sample is weighed and fractionated according to the ECD capacity (approximately 100g). The bituminous mass used for the trials are shown in Table 4.

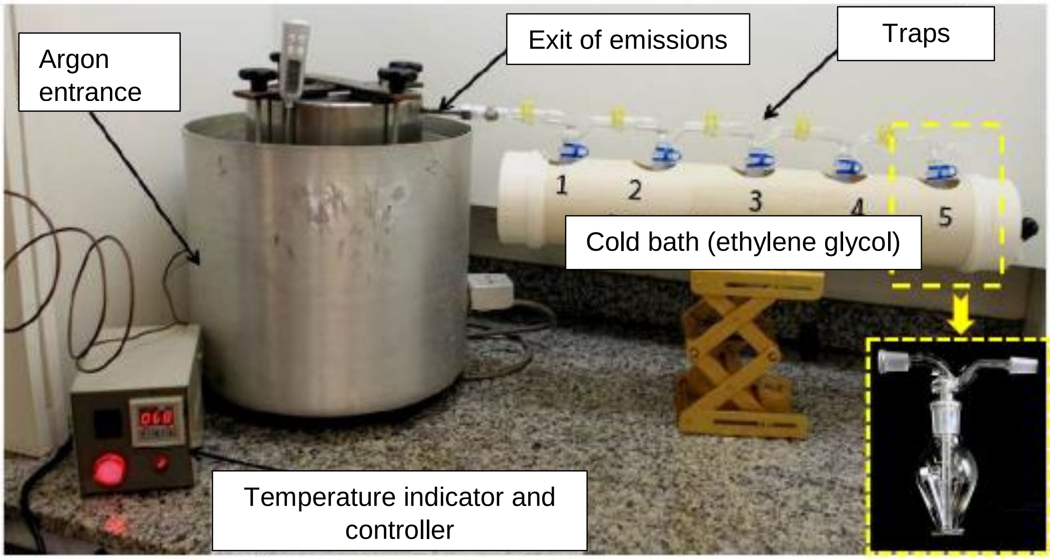

Figure 3: ECD photograph. Font: Ferraz, 2015.

The trial is done in order to try to approach at its best the reality found in road works, where first the asphalt is mixed and applied later. Similarly, the samples went through the following procedure: A sample of bitumen is placed in ECD. The ECD is set with the mix temperature indicated by the supplier. After 4 hours of heating and extracting fumes in the mixture temperature, the traps with adsorbed fumes are removed from the system. Without removing the sample from the bitumen that has been heated in the mix temperature, a new trap system with adsorbent is added to the system. The ECD is set to the application temperature of the bitumen as indicated by the supplier, and the extraction of fumes in the application temperature last over 4 hours. Then, the ECD is finally turned off and the traps are removed. The liquid held in the traps containing the adsorbed fumes are brought to filtering, making the samples become more translucent. The two treated samples (trials with mix and application temperature) are introduced into the LC-MS for quantizing and further quantifying of PAHs.

4. RESULTS

The results obtained by ECD in laboratory trial are the amount and what types of PAHs contains each bitumen. Through the extraction and collection of the fumes carried out in accordance with the ECD procedure described, through the use of LC-MS it was possible to reach the quantification of the results (in mg/kg) of each species of PAHs according to Table 5. Temperatures are shown in the tables in the order of the trial, first the mixing temperature and after the application temperature for the same sample.
The results are shown in mg/kg, a unit commonly used for these types of compounds. Unit changes can be made through physical and mathematical equations. In this work, in which the objective is to demonstrate the emissions at different temperatures and compare them, it will not to be necessary change units.
In the Table 5 "nd" means not detected by the method. These values were not found by the LC-MS analysis because they are very low, so will not be considered for the result analysis. Among the 14 PAHs that the procedure was able to detect, the six PAHs to be analyzed during the discussion are: Fluorene (Flu), Acenaphthalene (Ac), Acenaphthene (Ace), Naphthalene (Na), Fluoranthene (FL) and Anthracene (An). The PAHs that were not detected or were below the limit of quantification are: Phenanthrene (Ph), Pyrene (Py), Benzo [b] fluoranthene (BbF), Benzo [k] fluoranthene (BKF), Benzo [a] pyrene (BaP), Dibenzo [a, h] anthracene (DA), Benzo [g, h, i] perylene (BPE) and indeno [1,2,3-cd] pyrene (IP) and will not be shown in the result tables.

Table 5: Emission Results of PAHs species (mg / kg) detected above the limits of quantification in the main bitumen used in Brazil in the mixing and application temperatures.

Sample Identification	Mix/ Application Temperature	Flu	Ac	Ace	Na	FL	An
Hard Cap	168	1,9	0,17	0,66	19,38	1,06	0,06
	158	0,98	0,13	0,37	11,16	3,69	0,02
50-70	152,5	2,18	0,12	0,06	0,08	0,73	0,01
	135	0,13	0,1	nd	0,31	0,7	0,01
30-45 B	154	0,48	0,1	0,09	0,23	0,73	nd
	144	0,17	0,14	nd	0,05	0,75	0,01
30-45 A	157,5	0,58	0,15	0,08	0,38	0,8	0,01
	140	0,16	0,21	nd	0,07	0,85	nd
TLA Modificado	158	0,28	0,1	0,23	1,31	0,64	0,01
	149	0,38	0,11	0,11	0,21	0,69	0,01
Flexpave (60-85)	162,5	0,32	0,11	0,11	1,26	0,86	0,01
	145	0,27	0,14	nd	0,08	0,85	0,01
Stylink (76-22)	163	0,19	0,1	0,15	0,71	0,62	0,01
	144	0,21	0,12	0,08	0,09	0,59	0,01
HIMA II	172,5	0,16	0,12	0,06	0,24	0,68	0,01
	162,5	0,45	0,11	0,09	0,34	0,69	0,03
HIMA I	173	0,28	0,11	0,17	1,05	0,92	0,01
	163	0,27	0,11	nd	0,17	0,89	0,01
TLA AM	174	0,1	0,07	0,05	0,1	0,4	0,01
	149	0,09	0,06	nd	0,07	0,41	nd
Ecoflex	175	0,46	0,1	nd	0,04	0,59	0,02
	150	0,62	0,11	nd	nd	0,59	0,01
Borracha	182,5	0,76	0,12	0,23	0,93	0,78	0,03
	162,5	0,6	0,11	0,15	0,18	0,79	0,01

For the discussion of results by type of PAHs graphics were generated with emission by type of bitumen, where emissions were divided into mixture (orange) and application (blue) temperatures.

The chose PAHs for the analysis in this stage of the work presented the most relevant results, above the detection limits. They are: Fluorene (Flu), Acenaphthalene (Ac), Acenaphthene (Ace), Naphthalene (Na), Fluoranthene (FL) and Anthracene (An).

By observing Figure 4, fluorene emission by bitumen according to the mixing temperature and application graphic, it is clear that most binders emit more fluorene in mix temperatures.

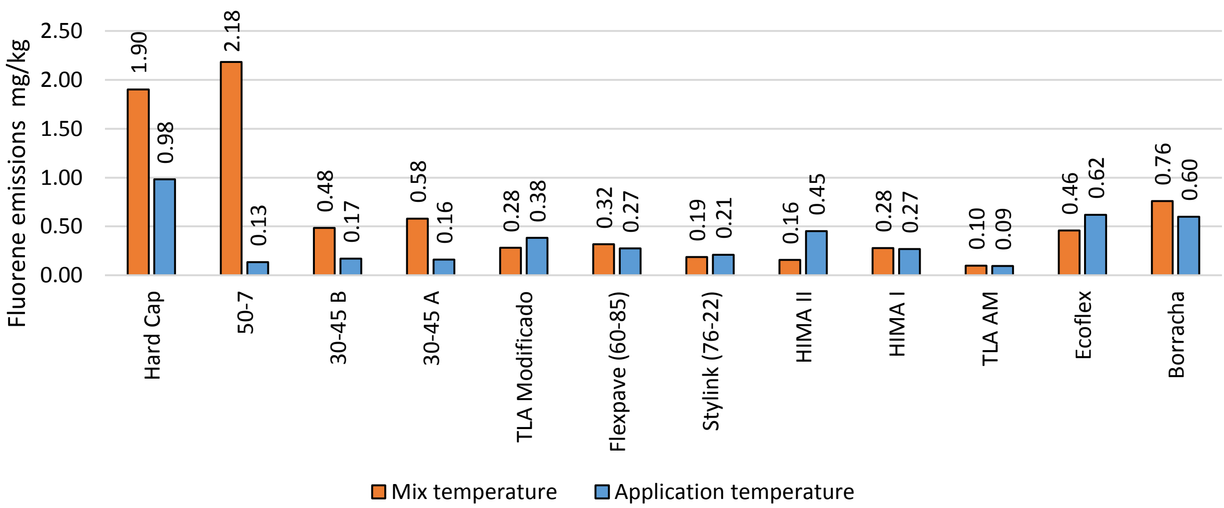

Figure 4: Comparative graph of Fluorene emission (mg / kg) bitumen and temperature.

It is important to say that the graphics are exposed in different scales. This occurred due to the difference between the proportions of amount of emissions from each PAHs. For example, the species of PAHs that had the highest value detected was fluorene with 2,18 mg / kg. The species with the lowest value, even below the detection limit, was benzo (a) pyrene with values close to zero, therefore this and other species with low detection rates were not analyzed graphically.

The Acenaphthylene emissions shown in the graph of Figure 5 were similar at both temperatures tested and relatively similar in all kinds of bitumen's.

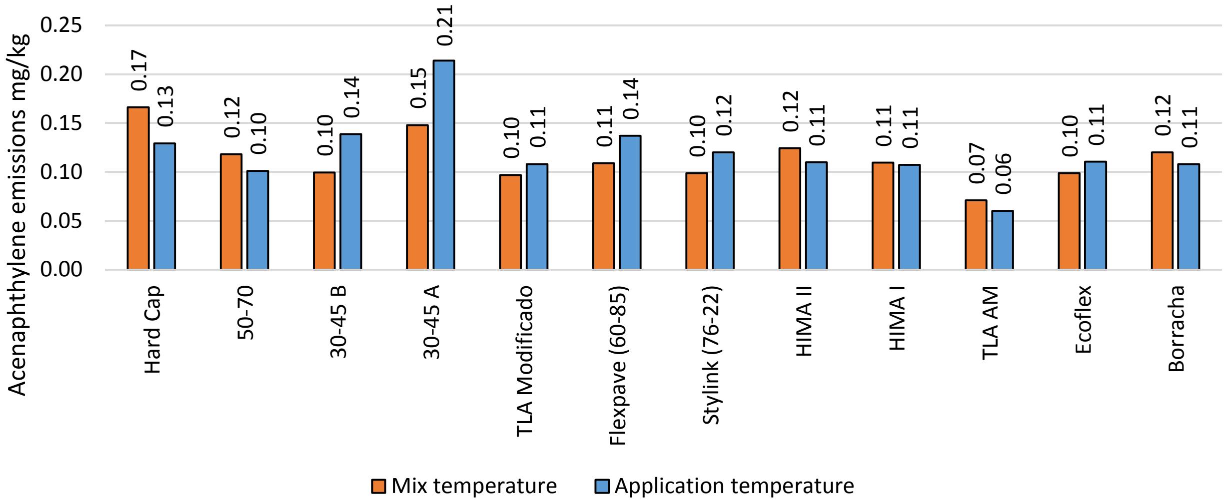

Figure 5: Comparative graph of Acenaphthylene emission (mg / kg) bitumen and temperature.

The Acenaphthene in general had low emissions compared with other PAHs. However, the Hard CAP presented high emission of this analyte. As you can see, Acenaphthene emissions were most frequent in mixing temperatures (higher). At application temperatures, some CAPs didn't produce perceptible amounts of Acenaphthene, as shown in the graph of Figure 6.

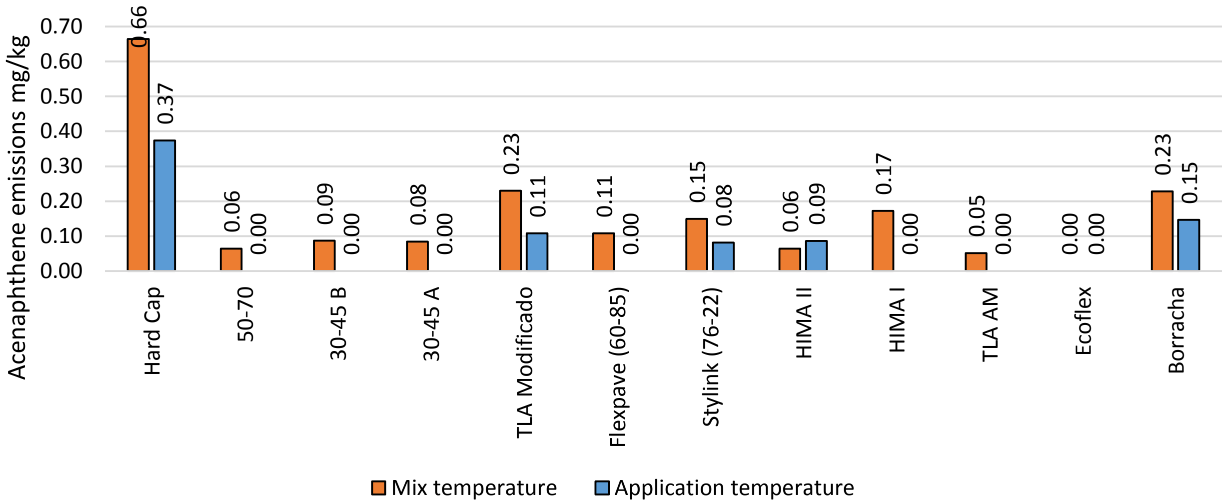

Figure 6: Comparative graph of Acenapthene emission (mg / kg) bitumen and temperature.

The Naphthalene was detected in this experiment, this is one of the most cited PAHs in scientific research on occupational health in various professional areas. The graphs of Figures 7 and 8 show emissions for the studied bitumen. It was observed that the emission of Naphthalene by Hard CAP is approximately 660% higher than the emission of this PAHs by Modified TLA, the second largest emitter of Naphthalene between the analyzed bitumen. For this reason, in the graph of Figure 9, the Hard CAP is removed to observe the behavior of the Naphthalene emission by other bitumen more clearly. Thus, it is possible to infer that emissions of Naphthalene do not follow a pattern according to the temperature.

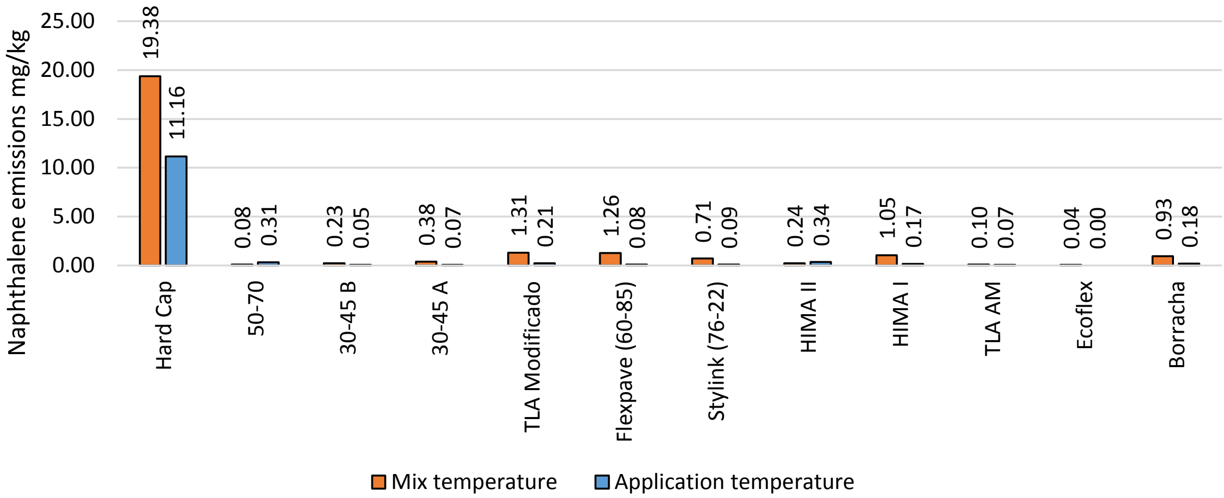

Figure 7: Comparative graph of Naphthalene emission (mg / kg) bitumen and temperature.

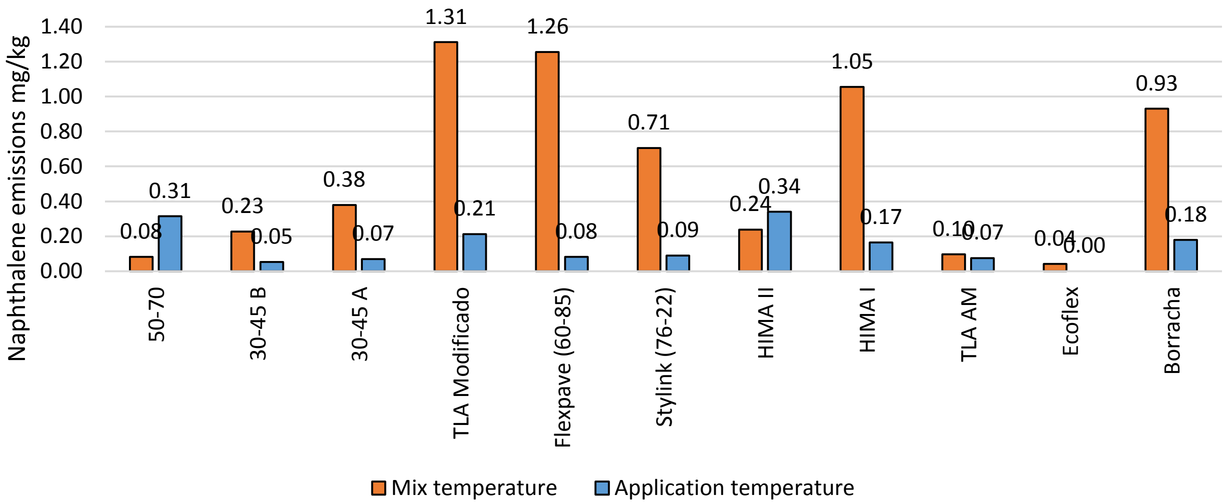

Figure 8: Comparative graph of Naphthalene emission (mg / kg) bitumen and temperature. The Hard CAP result was disconsiderer.

Anthracene emissions measured by LC-MS were also low. However, it's important to demonstrate the results where it is apparent the PAHs species diversity emitted by Brazilian bitumen, as can be seen in the Figure 9 graph.

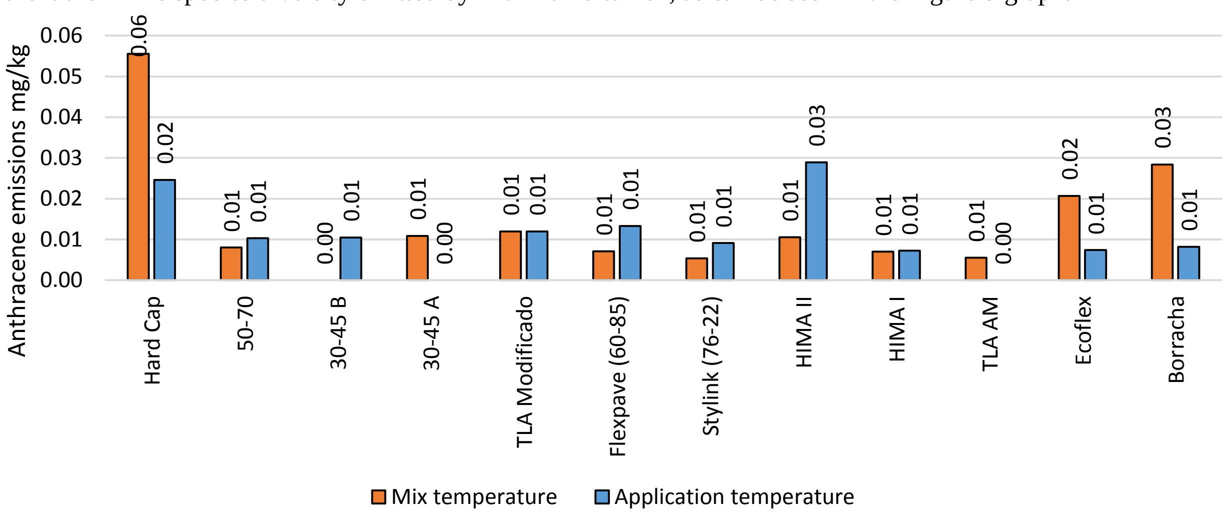

Figure 92: Comparative graph of Anthracene emission (mg / kg) bitumen and temperature.

Finally, the pattern of fluoranthene emissions were different from other PAHs species emission. As graph in Figure 10, the emissions were constant in eleven of the twelve Brazilian bitumen in both temperatures tested for each bitumen. Again it is noticeable the difference in Hard CAP emissions.

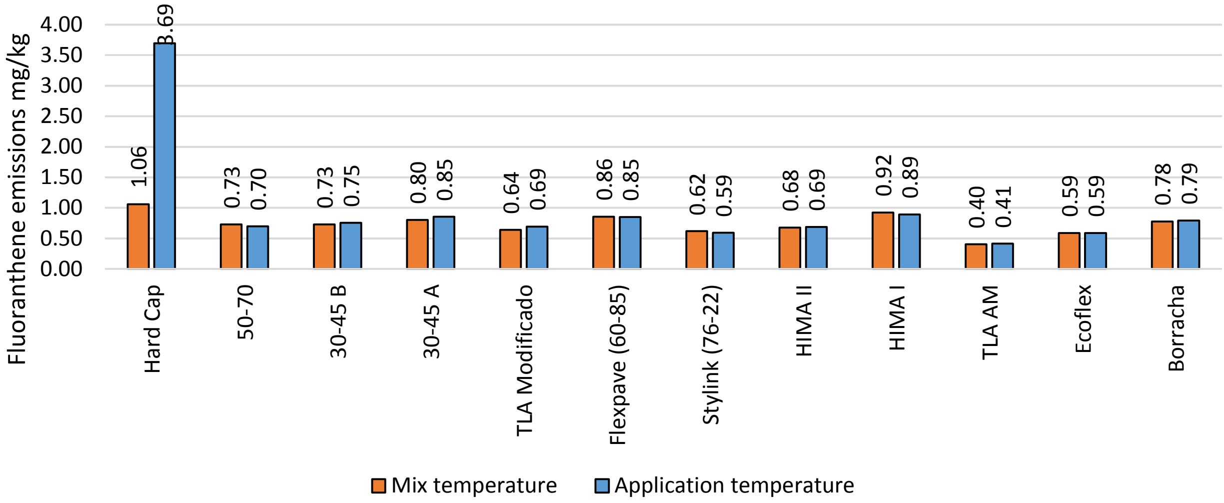

Figure 10: Comparative graph of Fluoranthene emissions (mg / kg) bitumen and temperature.

It is observed in all Graphs from Figures 4 to 10, that the CAP 30-45 from both suppliers have similar PAHs emissions. This comparison is relevant because the CAPs 30-45 are very similar materials and with have close behavior because they come from the same source before reaching the suppliers. The result uniformity for this kind of bitumen is an indication that the ECD and later the LC-MS analysis are efficient in extracting, collecting and analyzing bitumen PAHs emissions. However, there is no correlation to true workplace exposure.

Although the chemical composition is unknown, Hard CAP is a product commercialized in Brazil and was the material responsible by the highest emissions of almost all PAHs. There was a possibility that these emissions have been due to the high temperatures that are suitable for blending and compaction of the CAP, however, this assumption is not necessarily true since the CAP Rubber was subjected to higher temperatures than the Hard CAP and had lower emissions perceived in this research.

These observations lead to the conclusion that the temperature which the bitumen is subjected in the trial is as important as the characteristics of each material. However, it was clear that each type of material emits different amounts of PAHs, where emissions in mix temperature are higher. The temperature is a key factor when analyzing the same bitumen, however when compare the different bitumen emissions, the temperature diversify.

In this context, to graphically verify the assertion, one way was sum the species of PAHs in all bitumen types. However, each PAHs emission was on a different scale. For example, the maximum emission in the specie Naphthalene was 19.38 mg/kg (Figure 7), while the maximum value given by the Fluoranthene was 1.06 mg / kg (Figure 10). To be able to add the emissions of PAHs, they were organized as a ranking, as follows: The highest value of a PAHs was considered one and the lowest emission value of that PAHs was considered zero. Intermediate values were calculated in proportion to the new maximum (one) and minimum (zero).

Six PAHs were analyzed: Fluorene, Acenaphthylene, Acenaphthene, Naphthalene, Anthracene and Fluoranthene. Since the eight other PAHs have a very low detection range, next to the LC-MS measurement error (up to 0.03 mg / kg) they were not considered for this analysis.

It is important to emphasize that each bitumen studied was tested in a different temperature, according to Table 4. The graph was generated for both temperatures, mixing and application.

To analyze the results of the trial on application temperatures, it is pertinent to pay attention to the fact that when the bitumen was subjected to application temperatures in ECD, it had already passed through four hours extraction process in the mixture temperature.

Analyzing the graph contained in Figure 11, it is noted the mixing temperatures are higher than the application temperatures. Comparing both figures mentioned above, it is clear that at higher temperatures (mixture), more PAHs were emitted than in application temperatures. On Table 6, it can be seen the percentage relation of decrease between emissions in mix and application temperatures. The sum presented is the same used to generate the graph in Figure 11 where the largest value for each PAHs emission was considered as 1 and the lowest 0 (emissions ranking per species).

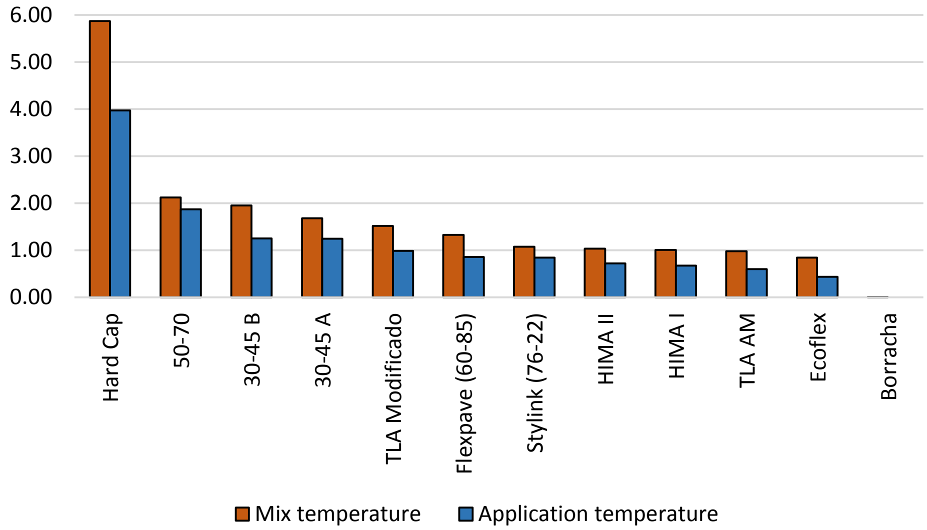

Figure 11: Comparative graph between the weighted sum of emissions in mixing and application temperatures.

Table 6 – Statement of percentage decrease of PAHs emissions in mix temperature for application temperature in the studied bitumen. The values shown in the table are from the aforementioned ranking.

Bitumen	Sum of emissions in mix temperatures	Sum of emissions in application temperatures	Percentage relation
Hard Cap	5,87	3,98	-32%
50-70	2,12	1,87	-12%
30-45 B	1,95	1,25	-36%
30-45 A	1,68	1,24	-26%
TLA Modificado	1,51	0,98	-35%
Flexpave (60-85)	1,33	0,86	-35%
Stylink (76-22)	1,07	0,85	-21%
HIMA II	1,03	0,72	-30%
HIMA I	1,01	0,67	-33%
TLA AM	0,98	0,60	-39%
Ecoflex	0,84	0,44	-48%
Borracha	0,0092	0,0029	-69%

5. CONCLUSIONS

Considering the importance of road transport in the Brazilian transport matrix, it was relevant to study the emissions that the main materials for road paving (bitumen) present. Emissions originated by heating the bitumen contain PAHs, the purpose of this study. PAHs are emitted in higher or lesser extent according to the characteristics and temperatures of the material. Emissions, although low, have an impact not well known on health and environment.
In this work the samples were analyzed representing the Brazilian bitumen market in a comprehensive way. The 12 bitumen whose emissions have been demonstrated are the main marketed and used materials in Brazil nowadays. Thus, the study spectrum was complete and served to demonstrate an innovative way, using methods of extraction, collection and analysis, the values of PAHs emissions of these bitumens. The ECD (extraction and collection device) is a device that generate and collect fumes in laboratory and there is no correlation to true workplace exposure.
The objectives were clearly reached, since the extraction and analysis at different temperatures of PAHs present in the main bitumens commercialized in Brazil through the ECD were performed and the results obtained.
To obtain the results, the ECD was used to promote the release and capture of asphalt fumes for further quantification of PAHs. With the quantized and organized results in tables, it was possible to verify the existence of differences between emissions of each type of PAHs for each of the 12 major bitumens commercialized in Brazil. Through this verification was viable to evaluate the importance of different temperatures which each bitumen is submitted.
The results obtained using LC-MS analysis after the trial in ECD were satisfactory, as they have shown proper operation of the ECD for these types of bitumens in compared results between two similar samples from CAP 30-45.
The analysis of the results concluded that in the mixing temperature the PAHs emissions are higher. For this reason, in the mixture temperature most species of PAHs was extracted in greater amounts by the ECD. However, it is plausible to emphasize that emissions of each bitumen cannot be directly related to the temperature. Hard CAP, for example, was subjected to lower temperatures (both mixing and application) than the Rubber bitumen. Still, the Hard CAP had considerably higher emissions than the Rubber bitumen. For the same bitumen, temperature is a key factor for PAHs emissions, it's possible to say that the higher the temperature the greater the emissions of PAHs. However, comparing the

emissions from different bitumens, it is not possible to say that the higher the CAP's temperature the greater the emission of PAHs. This statement serves to analyze each bitumen separately, as shown in Figure 11 and Table 6, where all the bitumen presented decrease in emissions as a function of temperature and ECD trial method (first emission removal in mixing temperatures and after emission removal of application temperatures).
Another interesting conclusion is that the modified bitumen, in general, do not have higher emissions than conventional bitumen, although with higher temperatures of mixing and compaction.

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