Emission of parent, nitrated and oxygenated polycyclic aromatic hydrocarbons from manually and automatically fired residential combustion appliances

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The organic fraction of particles released during residential combustion encompasses mutagenic compounds such as polycyclic aromatic hydrocarbons (PAHs) (Claxton et al., 2004; Oanh et al., 2002). In Portugal, it has been estimated that residential biomass combustion is responsible for approximately 6.5% of the total emissions of PAHs (Gonçalves et al., 2012). The combustion conditions may have greater effects on particulate-phase PAH emissions than on submicron particle emissions (e.g. Johansson et al., 2004).

A manual and batch operated stove burning wood logs and an automatic pellet stove were selected for the combustion experiments. Two types of firewood, pine and eucalypt, were used as fuel in the manual stove. Four types of pellets and three agricultural fuels (olive pit, almond shell and shell of pine nuts) were selected for the experiments in the automatic stove. Particulate matter sampling was carried out in a dilution tunnel under isokinetic conditions with a Gent PM_{10} stacked filter unit. The quantification of the parent-PAHs, nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs) was performed after solvent extraction using a GC-MS (Bandowe et al., 2014). In this study, 23 parent-PAHs, 11 NPAHs and 15 OPAHs were quantified.

The total parent PAH emission factors for the pellet stove ranged from 0.046 to 0.513 mg kg^{-1} of fuel (dry basis, db) burned. Retene was the PAH with the highest emission factor (EF) for almost all the fuels. Since retene is a pyrolysis product of resin acids in conifer woods it is not surprising that shell of pine nuts has presented the highest retene EF (250 mg kg^{-1} of fuel burned, db). The EF for this agro-fuel was followed by one type of pellets made almost entirely of pine wood with EN-Plus certification (137 mg retene $kg^{-1}$of fuel burned, db). The PAH emissions were also dominated by pyrene, phenanthrene and benzo[a]anthracene. The experiments performed in the wood stove generated PAH EFs ranging from 0.329 to 1.97 and from 8.65 to 24.3 mg kg^{-1} of fuel (db) burned, for the combustion of eucalypt and pine, respectively. The combustion of conifer logs are characterised by higher burning rates, which result in very hot flames and short, local drop of oxygen concentration during the combustion, leading to high emissions of PAHs. The dominant PAHs for eucalypt combustion were pyrene and benzo[a]anthracene. For pine combustion, retene was the dominant compound, followed by pyrene.

For the pellet stove experiments, the total OPAH EFs ranged from 0.004 to 1.90 mg kg^{-1} of fuel burned (db). Among the OPAHs measured, 9-fluorenone was present in all the samples. The experiments performed in the wood stove generated OPAH EFs ranging from 0.126 to 2.03 and from 1.64 to 10.3 mg kg^{-1} of fuel (db) burned, for the combustion of eucalypt and pine, respectively. The OPAHs emissions were higher during the devolatisation combustion phase for both fuels. For eucalypt, the devolatisation combustion phase generated high amounts of 1,8-naphthalic anhydride, whilst 9,10-anthraquinone dominated during the remaining combustion cycle. For pine combustion, the devolatisation phase was dominated by 9-fluorenone, whereas the flaming and smouldering combustion phases generated higher 1,8-naphthalic anhydride EFs.

For the pellet stove, the total NPAH EFs ranged from 0.027 (pellets of waste wood from furniture) to 0.158 (shell of pine nuts) mg kg^{-1} of fuel (db) burned. Excluding pellets with EN-Plus certification and shell of pine nuts, whose emissions contained 6-nitrochrysene, 5-nitroacenaphthene was the only NPAH detected in the remaining samples. The NPAH EFs for the experiments performed in the wood stove ranged from 0.204 to 0.891 and from 2.16 to 4.24 mg kg^{-1} of fuel (db) burned, for eucalypt and pine combustion, respectively. During the devolatilisation phase, the dominant NPAHs in smoke particles from eucalypt were 5-nitroacenaphthene and 2,7-dinitrofluoranthene. 5-Nitroacenaphthene and 6-nitrochrysene were prevalent during the flaming and smouldering phases. Softwood generated higher amounts of 5-nitroacenaphthene for the entire combustion cycle. The results indicate that both biofuel and combustion appliance may greatly affect the PAH EFs.

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