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Retene Emission from Residential Solid Fuels in China and Evaluation of Retene as a Unique Marker for Soft Wood Combustion

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Abstract

Retene (1-methyl-7-isopropylphenanthrene) is often used as a marker for softwood combustion and for polycyclic aromatic hydrocarbon (PAH) source apportionment. The emission factors of retene (EF_{RET}) from 11 crop residues, 27 firewood and 5 coals were measured using traditional rural Chinese stoves. Retene was measured in combustion emissions from all of the residential fuels tested and EF_{RET} varied significantly among the fuels due to the differences in fuel properties and combustion conditions. EF_{RET} for pine (0.34 ± 0.08 mg/kg) and larch (0.29 ± 0.22 mg/kg) were significantly higher than those of other wood types, including fir and cypress (0.081 ± 0.058 mg/kg). However, EF_{RET} for crop residues varied from 0.048 ± 0.008 to 0.37 ± 0.14 mg/kg and were not significantly lower than those for softwood (0.074 ± 0.026 to 0.34 ± 0.08 mg/kg). The EF_{RET} for coal were very high and ranged from 2.2 ± 1.5 (anthracite briquette) to 187 ± 113 mg/kg (raw bituminous chunk). EF_{RET} was positively correlated with EFs of co-emitted particulate matter (EF_{PM}) and phenanthrene (EF_{PHE}) for crop residue and coal, but not for wood. In addition, the ratios of EF_{PHE}/EF_{RET} and EF_{PM}/EF_{RET} for coals were much lower than those for crop residues and wood. These data suggest that retene is not a unique PAH marker for softwood combustion and that coal combustion, in particular, should be taken into account when retene is used for PAH source apportionment.

Keywords

Retene; Emission Factor; Wood; Coal; Crop Residue

Introduction

Like other parent polycyclic aromatic hydrocarbons (PAHs), retene (1-methyl-7-isopropylphenanthrene) is a product of incomplete combustion and is ubiquitous in sediments and atmospheric particulate matter^{1,2}. In 1983, it was reported that retene was

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Supporting Information **Available:** Fuel properties, combustion and sampling duration, combustion temperatures, calculated burning rates and MCE, EF_{RET} , EF_{PHE} and EF_{PM} , layout of the kitchen and pictures of stoves, composition profiles of co-emitted EPA 16 priority PAHs and relationship between PHE and total PAHs from residential crop residue, wood, and coal combustion were provided in the Supporting Information. These materials are available free of charge via the internet at <http://pubs.acs.org>.

detected in the smoke from spruce (*picea abies*) combustion, but not in the smoke from other firewood, even at high combustion temperatures and oxygen rich conditions³. Later, the presence of retene in pine wood smoke, but not in smoke from oak wood, was reported⁴. McDonald *et al.*⁵ compared retene emissions from softwood (*ponderosa pine and pinion pine*) and hardwood (*oak and mixed hardwoods*) combustion in fireplaces and wood stoves under different combustion conditions. They found that emission factors for retene (EF_{RET}, defined as mass of retene emitted from per fuel burned) from softwood combustion (1.79±0.30 mg/kg) were 4 times higher than those from hardwood combustion (0.50±0.22 mg/kg) in fireplaces and near 90 times higher than hardwood combustion in wood stoves (0.02±0.01 mg/kg)⁵. From these studies, it appeared that retene could be used as a marker for softwood combustion⁶. It was suggested that retene was formed primarily from the thermal degradation of abietic acid^{1,3}. This proposed mechanism of retene formation is very different from the formation of other parent PAHs, which are formed through pyrolysis and recombination of smaller molecular fragments through pyrosynthesis^{1,3}. Based on the high concentration of retene in smoke from softwood combustion and the proposed mechanism of formation, it was proposed that retene could be a useful marker for the combustion of conifer fuel with abundant diterpenoid resin acid³⁻⁶.

To be used as a molecular tracer in source apportionment, retene should be uniquely, or at least dominantly, emitted from conifer wood combustion. However, emissions of retene have been measured from non-softwood combustion and the uniqueness of retene as a marker for conifer wood combustion has been questioned⁷⁻⁸. For example, the EF_{RET} measured from the combustion of lignite and sub-bituminous coal, were 101 and 282 mg/kg, respectively⁹ and were high relative to the measurements from softwood combustion¹⁰⁻¹⁶. In addition, EF_{RET} values of 0.903 and 0.011 mg/kg were reported for the open burning of rice and wheat straw¹⁷ and retene was detected in the emissions of other fuels, including hardwood (oak, aspen and eucalyptus fuels)^{5, 10-11}, vehicle exhaust, and road dust⁸. In addition, one study found that there was no significant difference ($p > 0.05$) between indoor RET concentrations in Swedish homes with and without wood burning during the winter¹⁸. Similarly, no significant difference was found in retene concentrations in indoor air when wood or crop residues were used as cooking fuels in a rural household near Beijing¹⁹. Because retene is excluded in the USEPA priority pollutant list, it is not commonly measured or reported and emission factors for retene are very limited. Based on the current data available, it is difficult to evaluate the validity and usefulness of using retene as a tracer for conifer wood combustion and source apportionment.

The objective of this research was to systematically determine the retene emission factors from combustion of a variety of residential solid fuels in order to determine the usefulness of retene as a unique marker for conifer wood combustions and source apportionment. A series of combustion experiments were conducted to measure the retene emissions from a number of commonly used residential solid fuels, including 11 crop residues, 27 wood, and 5 coals using typical Chinese rural stoves (a cooking stove for crop residues and wood and a coal stove for coal). Of the 27 wood types burned, 5 were softwood. The EF_{RET} were calculated for the different residential solid fuels and the relationships between retene emissions and the co-emitted particulate matter (PM) and PAH emissions were investigated. In addition, the impacts of fuel properties and combustion conditions on retene emissions were assessed.

Method

Fuels and Combustion Experiment

Detailed information on the residential solid fuels tested and combustion facilities used have been previously reported²⁰⁻²². The layout of the kitchen was shown in the Supporting Information (Fig. S1). In brief, a traditional brick wok stove, used in kitchens throughout

rural China, was used for testing RET emissions from residential crop residue and wood combustion. For coal combustion, a movable cast-iron stove, purchased from the local market, was used. Eleven different crop residues and twenty-seven different wood fuels were tested, including straw of Broomcorn (*Sorghum Moench*), pea (*Pisum Linn.*), horsebean (*Vicia Faba*), peanut (*Arachis Hypogaea*), soybean (*Cassia Agnes*), cotton (*Anemone Vitifolia*), rice (*Oryza Sativa*), wheat (*Triticum Aestivum*), rape (*Brassica Napus*), sesame (*Sesamum Indicum*), and corn (*Zea Mays*), as well as Chinese white poplar (*Populus tomentosa Carr.*), water Chinese fir (*Metasequoia glyptostroboides*), Chinese pine (*Pinus tabulaeformis Carr.*), cypress (*Cupressus funebris Endl.*), elm (*Ulmus pumila L.*), fir (*Cunninghamia lanceolata*), larch (*Larix gmelini (Rupr.) Rupr.*), maple (*Acer mono Maxim.*), oak (*Quercus mongolica*), paulownia tomentosa (*P. tomentosa (Thunb.) Steud.*), toon (*Ailanthus altissima*), white birch (*Betula platyphylla Suk*), willow (*Salix babylonica*), locust (*Robinia pseudoacacia L.*), bamboo (*Phyllostachys heterocycla (Carr.)*), lespedeza (*Lepepeza bicolor. Turcz.*), holly (*Buxus megistophylla Lévl*), buxus sinica shrub (*Buxus sinica (Rehd. et Wils.) Cheng*), ribbed birch (*Betula dahurica Pall.*), paulownia elongate (*P. elongata S. Y. Hu*), Italian poplar (*Populus nigra L.*), China aspen (*Populus adenopoda Maxim.*), Chinaberry (*Melia azedarach*), and the trees of jujube (*Ziziphus jujuba Mill.*), persimmon (*Diospyros kaki Thunb.*), mulberry (*Morus alba L.*), and peach (*Prunus persica*). The five different coals tested included two honeycomb briquettes made of either anthracite from Beijing or bituminous from Taiyuan, and three raw bituminous chunks from Taiyuan and Yulin. Fuel properties, including moisture, C, H, N, and O content, volatile matter (VM) content, ash content, and higher heating values were measured²⁰ and provided in the Supporting Information (Table S1-S3). The mean C and VM were 48.0±1.1 and 80.9±3.1 % for wood, and 60.6±22.0 and 19.6±10.3 % for coals, respectively. The percent moisture of the crop residues, wood fuels, and coals were 3.59±1.98 % (1.41~7.87 % as range), 18.4±12.0 % (5.32~ 41.8 % as range), and 3.41±3.42 % (0.72~9.17 %, as range), respectively.

The combustion experiments were conducted following the daily cooking practice of the local residents. Pre-weighed crop residues (500~700 g) and wood fuels (~1.0 kg, in small pieces about 15~20 cm² × 20~30 cm in length) were inserted into the stove chamber sequentially. The coal stove was ignited outdoors using small wood chips and then moved into the kitchen and placed under a stainless hood. The smoke from both stoves entered a 4.5-m³ chamber with a built-in fan for mixing and the sampling and measurements were conducted in this region. The combustion experiments were done in duplicate for coal and crop residues and in triplicate for wood. Combustion durations and temperatures (for crop residue and firewood burning) were recorded, and the burning rates and modified combustion efficiencies (MCE, defined as CO₂/(CO+CO₂), on a molar basis) were calculated to quantitatively describe the combustion conditions (Table S4).

Sampling, Extraction and GC-MS Detection

CO and CO₂ concentrations were measured in the smoke every 2 seconds using an online non-dispersive infrared sensor (GXH-3051, Technical Institute, China) calibrated before each experiment using the span gas. Particulate and gas phase samples were collected on quartz fiber filters (QFFs) and polyurethane foam (PUF) plugs, respectively, using low-volume active samplers at a flow rate of 1.5 L/min. Sampling period covered for the whole burning cycle which lasted for 15-30 min for crop residues, 40-60 min for wood combustion, and 50-300 min for coals (Table S4).

The sample extraction, cleanup, and retene measurement methods have been previously described²². Briefly, the PUF plugs were extracted with 150 mL dichloromethane for 8 h and the QFFs were extracted with 25 mL hexane/acetone mixture (1:1, v/v) using a microwave accelerated system (CEM Mars Xpress, USA, 1200 W). The microwave

accelerated system temperature program was ramped to 110°C in 10 min and held for an additional 10 min. After the extraction, the extracts were concentrated to approximately 1 mL and transferred to a solid phase gel column for cleanup (12 cm silica, 12 cm alumina, and 1 cm anhydrous sodium sulfate from bottom-up, pre-eluted with 20 mL hexane). The column was eluted with 70 mL of a hexane/dichloromethane mixture (1:1, v/v) and the eluent was concentrated to 1 mL, with 200 ng deuterated internal standards (Chrysene-*d*₁₂, J&W Chemical Ltd., USA) added.

A gas chromatograph (GC, Agilent 6890) equipped with a HP -5MS capillary column (30 m × 0.25 mm × 0.25 μm) and connected to a mass spectrometer (MS, Agilent 5973) was used to measure retene. The GC oven temperature was held at 50°C for 1 min, increased to 150°C at a rate of 10°C/min, increased to 240°C at a rate of 3°C/min, and held at 280°C for 20 min. The carrier gas is He. Retene was identified and quantified based on its retention time and abundance of selected ions (*m/z* = 219) compared to a pure retene standard (J&W Chemical Ltd., USA).

Quality Control and Data Analysis

Blank concentrations of retene were measured using the same protocol and retene blank concentrations were subtracted from retene concentrations measured in the samples. The instrumental detection limit (IDL, defined as 3 times signal to noise ratio), method detection limit (MDL, defined as 3.14 times the standard deviation of 7 replicate analyses of spiked samples), and retene recoveries were determined before sample analysis. For gaseous and particulate phase retene, the IDL was 0.31 ng, the MDLs were 0.73 ng/mL and 0.40 ng/mL (equivalent to about 0.26 μg/kg), respectively, and the spiked recoveries were 104±24 and 100±18%, respectively. In laboratory, *p-terphenyl-d*₁₄ (J&W Chemical, USA) was added as a surrogate to monitor the analysis procedure, and surrogate recoveries were 85.2-98.8% and 81.9-87.5% for gaseous and particle phase samples, respectively.

Before sampling, the PUF plugs were pre-extracted sequentially with acetone, dichloromethane, and hexane for 8 hours each. The QFFs were pre-baked at 450°C for 6 h and stored in desiccators for 24 h before weighing and sampling. After sampling, the PUF plugs and QFFs were wrapped in aluminum foil, transported to the laboratory, and stored at -20°C until analysis. The silica, alumina, and anhydrous sodium sulfate were pre-baked for 6 h, activated at 300°C for 12 h, and deactivated with deionized water (3%, w/w) before use. All glassware was cleaned in an ultrasonic cleaner and baked at 450°C for at least 10 h.

Retene emission factors were calculated based on the carbon mass balance method, assuming that the total carbon burned was emitted in the form of gaseous CO₂, CO, total hydrocarbon, and total carbon in particulate matter. Details of this calculation procedure have been previously published²⁰. Statistica (v5.5, StatSoft) was used for data analysis and a significance level of 0.05 was adopted.

Results and Discussion

Retene EFs for Residential Solid Fuel Combustion

The measured dry basis EF_{RET} for 11 crop residues, 27 wood fuels, and 5 coals are shown in Fig. 1 as means and standard deviations. The detailed data are provided in Table S5 together with a summary of the literature reported EFs. For the crop residues, EF_{RET} ranged from 0.083±0.007 (*pea straw*) to 0.37±0.14 (*rape straw*) mg/kg, with a mean and standard derivation of 0.14±0.10 mg/kg. Relatively high PM and PAH emissions were reported for rape straw burning in a previous study and it was suggested that these high emission rates were due to the relatively low moistures and consequently low combustion efficiencies²⁰. Hays *et al.* measured EF_{RET} from open burning of rice and wheat straws and reported EF_{RET}

of 0.90 and 0.01 mg/kg, respectively¹⁷. In this study, EF_{RET} for rice and wheat straws were 0.12±0.06 and 0.21±0.09 mg/kg, respectively. Generally, this type of residential cooking stove produced high emissions of PM and PAHs because of the limited oxygen supply²²⁻²³.

Similar to the crop residues, wood EF_{RET} varied dramatically among different tree species, ranging from 0.016±0.006 (*China Aspen*) to 0.34±0.08 mg/kg (*Chinese Pine*). In the literature, EF_{RET} for wood combustion ranged from 0.0042 to 46 mg/kg, depending on the species (e.g. softwood vs. hardwood), combustion facilities (fireplace vs. woodstove), and combustion conditions^{5, 10-20}. In this study, EFs of retene for softwood (0.20±0.11 mg/kg) were significantly higher than for hardwood (0.075±0.043 mg/kg) ($p < 0.05$). This difference has been reported in the literature¹⁴⁻¹⁶ and it was suggested that RET can serve as a biomarker for softwood combustion^{1-5, 14-16}. The means and standard deviations of EF_{RET} for softwood and hardwood combustion reported in the literature were 3.2±1.1 and 0.049±0.058 mg/kg in woodstoves, respectively, and 13±15 and 0.64±0.96 mg/kg in fireplaces, respectively (Table S5). Based on the literature data summarized in Table S5, the EF_{RET} for both softwood and hardwood combusted in fireplaces were higher than those combusted in woodstoves. Similar differences were also reported for carbonaceous particle emissions¹⁵. Among the five softwood species tested, the highest EF_{RET}s were measured for pine (0.34±0.08 mg/kg) and larch (0.29±0.22 mg/kg), followed by cypress (0.14±0.05 mg/kg) and water Chinese fir species (0.14±0.09 mg/kg). Relatively high EF_{RET} for pine compared to those for other softwood species such as fir, spruce, and hemlock are also reported in the literature¹²⁻¹⁵.

EF_{RET} for the different coals measured in this study ranged from 2.2±1.5 (anthracite briquette, Beijing) to 187±113 (bituminous chunk, Yulin) mg/kg, with a coefficient of variation (CV) of 153%. This CV was greater than the CV for crop residues (64%) and wood (78%). The relatively low EF_{RET} values for coal were measured from the two honeycomb briquettes with VM of 3.99 and 14.7%, while the retene emission of the other three bituminous raw chunks with VM of 22.8~28.0% were much higher (from 30±15 to 187±113 mg/kg). The EFs for retene and other PAHs for different coal types have been reported in the literature. For example, EF_{RET} was measured in lignite and sub-bituminous coal combustions at 101±2 and 282±45 mg/kg, respectively, but retene was not detected in brown and bituminous coal combustion emissions⁹.

Retene is often thought to be formed from the thermal degradation of diterpenoid precursors that are ubiquitous components of higher order vegetation and widely present in the geosphere^{3, 24-26}. A number of diterpenoid compounds were measured as either natural or alteration products in hardwood and softwood species²⁴⁻²⁵. The dehydration of abietic acid to dehydroabietic acid, then to dehydroabietin under decarboxylation conditions, and final formation of RET under full aromatization is believed to be the pathway of retene formation during coal combustion⁹.

Influence of Fuel Properties and Combustion Condition on EF_{RET}

In addition to significant differences among fuel types (crop residues, wood, or coal), EF_{RET} varied significantly within fuel types. CVs in those repeat measurements of crop residue, wood and coal were 27±18, 43±24, and 40±27 %, respectively. These EF_{RET} differences can be traced to differences in fuel properties and combustion conditions. The influence of fuel properties and combustion conditions on the emission of other incomplete combustion by-products, including other parent PAHs and PM were demonstrated and quantified in our previous research²⁰⁻²². We determined that fuel moisture and VM content, as well as MCE, were key factors for controlling the EFs of parent PAHs and particulate matter²⁰⁻²². In this study, these parameters were also measured and investigated to determine their influence on EF_{RET}.

For crop residues, significantly negative correlations between EF_{RET} and fuel moisture ($r = -0.596$, $p = 0.002$) and between EF_{RET} and MCE ($r = -0.415$, $p = 0.027$) were identified. These properties were also the strongest influencing factors affecting emissions of other parent PAHs and PM from crop residue combustion²⁰⁻²¹. An increase in moisture content may cause the generation of more free radicals, as well as a decrease in the combustion temperature and thermal degradation, resulting in the suppression of retene formation during combustion²⁷. In addition, under relatively low moisture conditions, fuel may burn fast enough to result in oxygen deficient conditions that lead to incomplete combustion and high emissions of various combustion byproducts¹. This is particularly true for residential stove combustion where the volumes of the combustion chamber and air supply are often limited²³. A negative correlation between MCE and EFs of pollutants, including PM and PAHs, have been previously reported^{22-24, 28} and MCE can be influenced by moisture, oxygen supply, and the residence time of air in the combustion chamber²⁸⁻²⁹.

In this study, when softwood and hardwood were burned, there was no significant correlation between EF_{RET} and moisture, VM content, and MCE ($p > 0.05$). Although EF_{RET} were significantly different among the hardwood and softwood tested, there was no significant difference between hardwood and softwood in fuel properties, including density, moisture, elemental and proximate analysis, and combustion conditions (Table S3). However, VM and MCE significantly influenced the EFs of co-emitted PM and other parent PAHs ($p < 0.05$). It may be that the concentrations of natural diterpenoids and triterpenoids in the wood play a larger role in determining EF_{RET} than these other variables²⁴⁻²⁶ and that the formation of RET from wood combustions is different from other parent PAHs^{1-15,30-33}.

For coal, EF_{RET} was found to be positively correlated with VM content ($r = 0.900$, $p = 0.019$). Positive correlations between coal VM content and EFs of PM, black carbon, and other parent PAHs were also reported in the literature^{22, 34}. It has been suggested that, when coals with higher VM content are burned, it is more difficult to achieve complete combustion and that more pollutants are emitted due to incomplete combustion³⁴. The two low EF_{RET} coals also had relatively low VM content and were the honeycomb briquettes. In addition to the low VM content, EF_{RET} reduction in coal may also be due to binding effects of clay elements added to the briquettes, which can accelerate VM combustion and catalyze the cracking process of coal tar³⁵. Relatively low EFs from briquette combustion was also reported for PM, black carbon, and PAHs^{22, 35}.

Correlation between EFs of Retene and Co-emitted Pollutants

The ratios of paired PAH isomers are often used to identify emission sources³⁶⁻³⁷. It has been proposed that retene can serve as a biomarker of PAH emission from softwood combustion¹⁻³. Therefore, it is interesting to compare the EFs of retene to other parent PAHs from the same solid fuels. To do this, phenanthrene was selected as a representative compound to retene for the following reasons: 1) The molecular structure of phenanthrene is similar to retene; 2) It is one of the most abundant PAHs among the often measured 16 parent PAHs (US EPA priority pollutants) (Fig. S2), and 3) Concentrations of phenanthrene are often correlated to the sum of the 16 parent PAHs (Fig. S3). Therefore, EF_{RET} was directly compared to the EF for phenanthrene (EF_{PHE}).

During the combustion experiments, 16 parent PAHs, including phenanthrene, were measured simultaneously with retene and we can compare EF_{RET} and EF_{PHE} ²⁰⁻²². The relationship between EF_{RET} and the EF for particular matter (EF_{PM}) was also evaluated because PM is an important co-emitted pollutant and a fraction of the retene emitted during combustion is associated with particles.

Fig. 2 shows that EF_{RET} vs. EF_{PHE} and EF_{RET} vs. EF_{PM} are significantly positively correlated for crop residues and coal emissions ($p < 0.05$). However, there were no significant correlations for residential hardwood or softwood ($p > 0.05$). EF_{RET} for crop residues are significantly affected by fuel moisture and MCE, which are also critical factors affecting EF_{PHE} and EF_{PM} from crop residues²⁰⁻²¹. In addition, EF_{RET} for coal was associated with VM content and this same correlation was reported for EF_{PHE} and EF_{PM} ^{20,22}. These similarities in influencing factors may imply that the mechanisms for generating retene and phenanthrene, pyrolysis and pyrosynthesis, are similar^{23,30} or that there are different mechanisms that are affected by the same influencing factors. However, for wood combustion, the major fuel properties and combustion conditions tested in this study, including moisture, MCE, and VM, were not correlated with EF_{RET} .

Although EF_{RET} for both crop residues and coals were correlated with EF_{PHE} and EF_{PM} , the difference between crop residues and coal was clear. At the same levels of EF_{RET} , EF_{PHE} and EF_{PM} , crop residues emissions were approximately 7 to 9 (EF_{PM}) and 3 to 5 (EF_{PHE}) orders of magnitude higher than coal emissions. EF_{RET} from coal were much higher EF_{RET} for biomass burning. Although there was no correlation between EF_{RET} and EF_{PHE} or between EF_{RET} and EF_{PM} for wood, the ratios of EF_{RET}/EF_{PHE} and EF_{RET}/EF_{PM} for wood were comparable to those for crops. These same ratios were much higher in coal combustion. This difference between coal and biomass can also be seen in Fig. 1 and Fig. S4. Even for the two honeycomb briquettes made of anthracites, for which relatively low EF_{RET} were observed, the ratios of EF_{RET}/EF_{PHE} and EF_{RET}/EF_{PM} were significantly higher than the highest ratios for biomass ($p < 0.05$).

Implication

It has been reported that retene can be used as a biomarker for the combustion of conifer fuel containing abundant diterpenoid resin acids, the thermal degradation of which results in the formation of retene³. Although relatively high EF_{RET} were from the wood of Chinese pine (0.29 ± 0.22 mg/kg) and larch (0.34 ± 0.08 mg/kg), EF_{RET} for the other three softwood fuels (0.13 ± 0.09 , 0.14 ± 0.05 , and 0.07 ± 0.03 mg/kg for redwood, cypress, and fir, respectively) were not significantly higher than those of many hardwood and crop residues. The mean EF_{RET} for Chinese pine and larch were lower than, but not statistically different from, the mean EF_{RET} for rape straw (0.37 ± 0.14 mg/kg) and not significantly higher than EF_{RET} for a number of crop residues, including straw of peanuts, corn and wheat (Fig. 1). Moreover, EF_{RET} for coals (from 2.2 ± 1.5 to 187 ± 113 mg/kg in this study, and 101 to 282 mg/kg in the literature⁹) were orders of magnitude higher than those of Chinese pine and larch (Fig. 1). The EF_{RET} reported in the literature for both softwood and hardwood varied under different combustion conditions (Table S5). Under similar conditions, pine often had higher EF_{RET} than fir and spruce species. Fine *et al.* reported unquantifiable levels of RET emitted from Douglas fir combustion and suggested that the emission of Douglas fir may be different from other softwood species¹⁴. In addition to fuel type, EF_{RET} also depends on combustion conditions (such as oxygen supply and combustion temperature) and fuel composition, especially those can serve as retene precursors, leading to high variations amongst the same fuel type (such as coal).

In addition to the thermal degradation of diterpenoid resin acids, other mechanisms of retene formation have been reported in the literature. For example, it has been suggested that retene can be formed during the maturation of phyllocladane and/or kaurane-type compounds and abiogenic cyclisation and rearrangement of bicyclic terpenoids². The emission of retene from traffic has also been measured⁸. All of these suggest that retene is not a unique biomarker for conifer emissions and that the emissions of retene from coal combustion, in particular, should be taken into account.

There were correlations between EF_{RET} and EF_{PHE} and between EF_{RET} and EF_{PM} for coal and crop residues, but not for wood. Although PM emissions were compared to retene emissions, EF_{RET}/EF_{PM} is unlikely to be a good combustion source indicator because the fate of PM is very different from the fate of retene and other PAHs. The ratios of EF_{PHE}/EF_{RET} and EF_{PM}/EF_{RET} for wood were similar to those for crop residues, but very different from those for coals. As shown in Fig. 3, both EF_{PHE}/EF_{RET} and EF_{PM}/EF_{RET} for coal (0.33 to 1.04 and 0.01 to 0.13) were 1-2 orders of magnitude lower than those for crop residues (23 to 93, 33 to 108) and wood, including softwood (4 to 311, 2 to 121), because of the high EF_{RET} for coal. When the EF_{RET} and EF_{RET}/EF_{PHE} from this study were combined with those reported in the literature, similar results were obtained (Fig. S5).

As more data on EFs for PAHs become available for different residential fuel types and combustion conditions, unique PAH markers or ratios may become evident. However, currently, there is significant overlap among different residential fuel types and no unique PAH combustion source biomarker or ratio exists. In addition, PAH isomers undergo different physical and photochemical processing in the atmosphere and a unique ratio might change significantly between emission and measurement in the atmosphere. Additional studies, especially field investigations on source receptor relationships, should be conducted before specific PAH biomarkers can be generally used.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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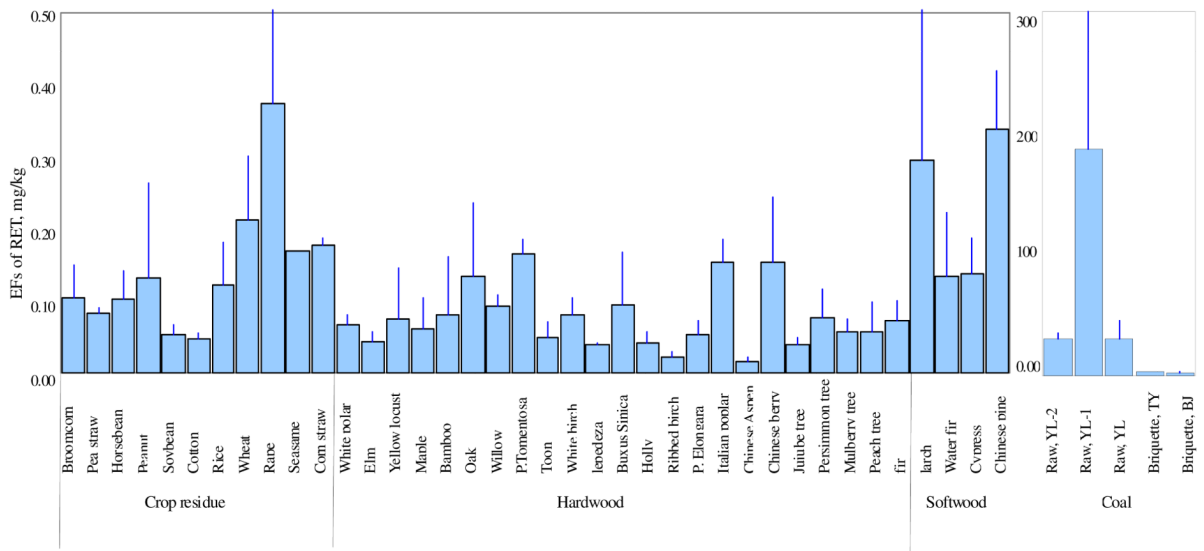


Fig. 1. Measured EF_{RET} (mg/kg, dry basis) for wood, crop residue, and coal combustion tested. The results are presented as arithmetic means and standard deviations.

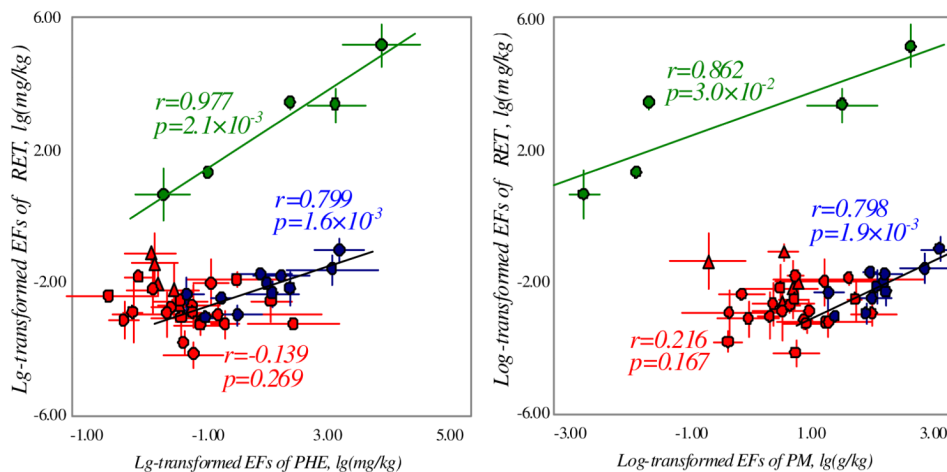


Fig. 2. Correlations between $\log EF_{RET}$ and $\log EF_{PHE}$ (left panel) and between $\log EF_{RET}$ and $\log EF_{PM}$ (right panel). The three fuels tested are marked separately using red (wood), blue (crop residues), and green (coal). Hardwood (circles) and softwood (triangles) are distinguished using different symbols. Data shown are means and standard variations from duplicate (crop residue and coal) or triplicate (wood) experiments.

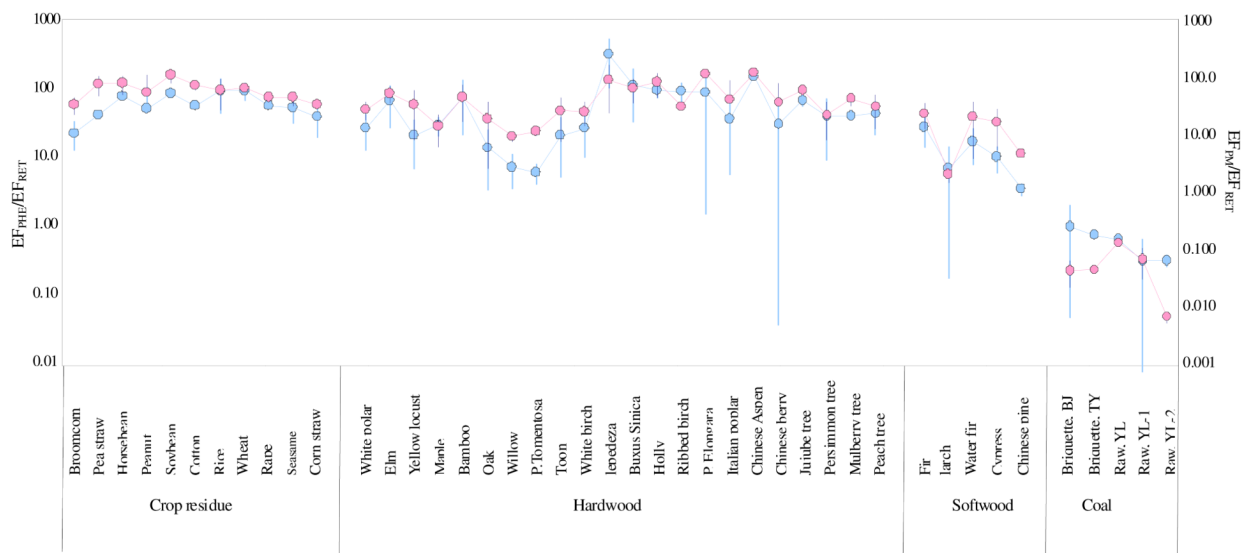


Fig. 3. EF ratios (EF_{PHE}/EF_{RET} (blue cycles) and EF_{PM}/EF_{RET} (red cycles)) in this study for crop residue, hardwood, softwood and coal. The results are presented as arithmetic means and standard deviations.