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# Polycyclic aromatic hydrocarbon (PAH) content of soil and olives collected in areas contaminated with creosote released from old railway ties

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**Abstract**

Simple sample preparation procedures involving sonication and solid phase extraction (SPE), followed by reversed-phase high performance liquid chromatography (HPLC) and spectrofluorometric detection, were used to analyse polycyclic aromatic hydrocarbons (PAHs) in soil and olives collected in areas contaminated with creosote-treated railway ties. Very high PAH contents (with amounts ranging from 114.7 to 2157.2 and from 167.3 to 3121.8 μg $kg^{-1}$ dry weight for total light PAHs and total heavy PAHs, respectively) were found in soil sampled up to 1 m from the source of contamination. The PAH load decreased rapidly with the distance from the railway ties. High amounts of light PAHs, up to 6359.9 μg $kg^{-1}$, were also found in oil extracted from olives collected in a rural area where old railway ties were stored. No appreciable transfer of heavy PAHs and benzo[a]pyrene was observed in oil samples.

*Keywords:* PAHs; Creosote; Reversed-phase HPLC; Soil; Olive oil; Railway ties

## 1. Introduction

Creosote is a complex mixture of over 200 compounds, predominantly polycyclic aromatic hydrocarbons (PAHs), as well as phenolic and aromatic nitrogen and sulphur compounds, obtained by fractional distillation of crude coal tar. It can contain over 30 different PAHs with a possible total PAH content of 85% by weight (World Health Organization, 2004). Chemical composition of creosote depends on the origin of the coal and the nature of the distillation process. Phenanthrene (Pa) is by far the predominant PAH followed by naphthalene (Na) and fluoranthene (Fl) (Bestari et al., 1998; Lehto et al., 2000).

Creosote is principally and almost exclusively used as an impregnation agent for outdoor wood structures such as: railway ties, poles for electrical power transmission, marine pilings, fences, stakes for agriculture and fruit production and equipment for children's playgrounds.

The production of creosote in the European Union (EU) has been estimated to be approximately 60,000–100,000 t per year (World Health Organization, 2004). According to the Priority Substances List Assessment Report of the Canadian Environmental Protection Act (Canadian Environmental Protection Act, 1993), preservation of railway ties uses 54% of the creosote. Depending on the type of wood, amount of creosote between 40 and 175 kg $m^{-3}$ of wood are pressed into the railway ties by the vacuum-high-pressure method (Rotard and Mailahn, 1987).

A number of papers has been published on PAH content of creosoted wood (Bergqvist and Holmroos,

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1994; Gagne et al., 1995; Gurprasad et al., 1995; World Health Organization, 2004). From these works it comes out that very high concentrations of PAHs remain in the wood even after several decades of use. Benzo[a]pyrene (BaP) concentrations up to 1573 and 656 mg kg$^{-1}$ shavings were found in railway ties installed in German playgrounds (Rotard and Mailahn, 1987) and in ties that had been in service for more than 60 years, respectively (Gurprasad et al., 1995).

Some PAHs pose a human health threat due to their carcinogenic and genotoxic properties. Among the 16 US-EPA PAHs, which include 2–6 rings compounds, only the 8 higher boiling PAHs (4–6 rings) have been recently recognised as carcinogenic and genotoxic compounds (European Commission, Opinion of 4 December , 2002). Among these, BaP and benz[a]anthracene (BaA) have the highest carcinogenic potential. BaP is often used as a marker of the presence of carcinogenic PAHs.

Due to the concerns regarding the carcinogenic potential of creosote, the EU has recently adopted Directive 2001/90/EC (Commission of the European Communities, 2001) introducing new restrictions on the marketing and use of creosote for wood treatment and creosote-treated wood. According to this Directive only creosote containing BaP at concentration of less than 50 mg kg$^{-1}$ may be used for wood treatment in industrial installations. Furthermore, creosoted wood may be used only for professional and industrial applications, and all amateur uses of creosote are prohibited.

PAHs, especially the lighter fraction, are slowly released from creosoted wood by oil exudation, rainwater (or irrigation) leaching and volatilisation (Behr and Baecker, 1994; Gurprasad et al., 1995; Gevao and Jones, 1998; World Health Organization, 2004). Concentrations up to several thousand mg kg$^{-1}$ dry weight for total PAHs have been found in soils from storage areas for disused railway ties. BaP concentrations found in soils near wood treatment/storage sites reached a maximum of 390 mg kg$^{-1}$dry weight (Canadian Environmental Protection Act, 1993).

Physicochemical properties of different PAHs, matrix characteristics, the presence of degrading or accumulating micro organisms and environmental conditions can largely influence the fate of creosote components that can be volatilised into the atmosphere or leached to water and soil. Some PAHs are easily degraded via biotic (aerobic and anaerobic) and abiotic processes; however, many heavy PAHs are recalcitrant and may persist in soil for many years. Within PAHs, degradability appears to be inversely related to the number of aromatic rings (World Health Organization, 2004).

According to the literature, PAHs are taken up to a small degree by terrestrial plants (Kipopoulou et al., 1999; Howsam et al., 2000, 2001).

Different authors reported data of PAH uptake from highly contaminated soil by different vegetables demonstrating that the extent of PAHs uptake is specie-dependent (Kipopoulou et al., 1999; Fismes et al., 2002; Tao et al., 2004). However, measurements of the possible adsorption/deposition of PAHs in vegetables near creosote sources are not available from the literature (World Health Organization, 2004).

The aim of this work was to study the amount of PAHs released into soil from old railway ties stored in different sites and the possible transfer to vegetation (olives). As high levels of light PAHs were detected by chance in oil obtained from olives grown near a heap of out-of-service railway ties, we chose olives as a test vegetable. Furthermore, due to the high oil content in olives (on average 20%) and lipophylic nature of PAHs, olives can represent a higher risk for consumers than other vegetables.

## 2. Materials and methods

### 2.1. Reagents and standards

Hexane, dichloromethane, acetone and acetonitrile were of HPLC grade (Baker, Deventer, The Nederland). Water was purified with a Milli-Q System (Millipore, Bedford, MA, USA).

The standard PAH mixture, 610 M, in 1 mL of methanol/dichlorometane (Supelco, Bellefonte, PA, USA) consisted of: acenaphtene (Ac) (1000 μg/mL), Fl (200 μg/mL), Na (1000 μg/mL), BaA (100 μg/mL), benzo[b]fluoranthene (BbF) (200 μg/mL), BaP (100 μg/mL), benzo[k]fluoranthene (BkF) (100 μg/mL), chrysene (Ch) (100 μg/mL), acenaphthylene (Ap) (2000 μg/mL), anthracene (A) (100 μg/mL), benzo[g,h,i]perylene (BghiP) (200 μg/mL), fluorene (F) (200 μg/mL), Pa (100 μg/mL), dibenz[a,h]anthracene (DBahA) (200 μg/mL), indeno[1,2,3-cd]pyrene (IP) (100 μg/mL), pyrene (P) (100 μg/mL).

All the glassware was carefully washed and rinsed with distilled solvent (acetone and hexane) before use.

A standard reference material of contaminated industrial soil (LGC6140, LCG Promochem, Milan, Italy) with certified concentrations of several PAHs was used to verify the extraction efficiency of real polluted soil samples.

### 2.2. Sample collection

Sampling was carried out in three different sites. Site 1 was a domestic garden in a rural area. At this site different