

VI.

ATMOSPHERIC PERSISTENCE

Among other factors, the combustibility of tobacco components, insufficient supply of oxygen, and the existence of a temperature gradient in the burning cone, makes ETS a mixture of several thousand compounds. Due to the complex chemical nature of ETS, a discussion of the atmospheric persistence of the “mix” as a whole is not practical. However, there are data on the atmospheric reactions that occur to several groups of ETS-related chemicals. Therefore, in this chapter we provide a general discussion of what is known about the atmospheric persistence of chemical groups within ETS, including nicotine, N-Nitrosamines and PAHs.

Studies show that the combustion of cigarettes include at least three important types of reactions, including: pyrolysis, pyrosynthesis, and distillation (NIH, 1998). The result of these reactions is the production of thousands of gaseous and particle constituents. Eventually, this complex mixture undergoes additional chemical reactions as the mix is diluted with ambient air, yielding individual compounds with their own atmospheric lifetimes. According to the Morawska *et al.* (1997) chamber and indoor environment study, the lifetime of the mixture of ETS constituents in the air may be up to several hours depending on the air ventilation rate, humidity, and atmospheric conditions.

A. ATMOSPHERIC REACTIONS OF GASEOUS SPECIES

Gaseous ETS constituents can react in the atmosphere with other pollutants and sunlight to form new chemical species (see Table III-2 in Chapter III for a list of gaseous components found in ETS; Appendix A contains a comprehensive list). For example, 1,3-butadiene can initially react in the atmosphere with the hydroxyl radical (OH), nitrate radical (NO₃), and ozone (O₃) to form acrolein and formaldehyde (Atkinson, 1994; Skov *et al.*, 1992). Gaseous species may also transform into particle phase species. For example, gas phase ammonia can react with gaseous nitric acid to form particulate ammonium nitrate (Atkinson, 1995). Exposure to ammonium nitrate has been found to cause burning or irritation of eye and skin (ARB, 1997a). Alternatively, as ETS ages, semi-volatile constituents of ETS, such as nicotine and neophytadiene, may shift from particulate phase to the gaseous phase.

Gaseous ETS components primarily react with the following:

- Sunlight through photolysis
- O₃ (ozone)
- OH radical during the daylight hours
- NO₃ radical during the nighttime hours
- Gaseous nitric acid (HNO₃)
- Nitrogen dioxide (NO₂)
- Hydroperoxy radical (HO₂) mainly during afternoon/evening hours

Important reaction processes for most gas-phase organic compounds are photolysis and subsequent reaction with O₃, as well as the OH and NO₃ radicals. For a few compounds, one or more of the other reactive chemical species (HO₂, NO₂, and/or HNO₃) may react at significant rates. For example, HO₂ radicals react with formaldehyde, acetaldehyde, and glyoxal, NO₂ reacts with conjugated dienes, and gaseous HNO₃ reacts with the amines. Table VI-1 provides examples of the atmospheric lifetimes and the dominant removal processes for some of the gaseous species found in ETS.

Table VI-1

**Estimated Atmospheric Lifetimes
of Selected ETS Constituents**

	Dominant Removal Process	Atmospheric Lifetime
1,3 Butadiene	OH radical	2 hours ^{1/}
Acetaldehyde	OH radical	9 hours ^{1/}
Acrolein	OH radical	7 hours ^{1/}
Benzene	OH radical	10 days ^{2/}
Formaldehyde	Photolysis	4 hours
N-Nitrosodimethylamine	Photolysis	5 minutes
Toluene	OH radical	2.5 days
PAHs (gas phase)	OH radical	3-27 hours

Source: ARB, 1998.

^{1/} 12-hour average daytime (OH of 2.0x 10⁶ molecule/cm³)

^{2/} 1 day = 12-hour of OH of 2.0x 10⁶ molecule/cm³

Gaseous species absorbed by particles may be unavailable for further chemical reaction. Gaseous species adsorbed to particles may be degraded by photolysis and reaction with tropospheric O₃, dinitrogen pentoxide (N₂O₅), NO₂, HNO₃, nitrous acid (HNO₂), sulfuric acid (H₂SO₄), and hydrogen peroxide (H₂O₂).

B. ATMOSPHERIC REACTIONS OF PARTICULATE SPECIES

Particles in the range of 0.01-10 µm are often referred to as PM₁₀. Typically, all of the ETS associated particles fall in the range of between 0.01 and 1.0 µm (U.S. EPA, 1992). ETS contains particulate species which have their own atmospheric persistence rates based on the particle size. The two most important processes affecting particle ETS species in the atmosphere are:

- Dry and wet deposition (i.e., physical removal) of particles, and
- Atmospheric transformations of species adsorbed to the particles.

Dry deposition is broadly defined as the transport of air pollutants from the atmosphere onto surfaces in the absence of precipitation (Davidson and Wu, 1989; Seinfeld and Pandis, 1998). Major factors affecting dry deposition are atmospheric turbulence, chemical, and physical properties of the air pollutants and the nature of the depositing

surface. Particles in the size range of 0.05 to 1 μm are expected to reside in the atmosphere for long time periods and can be transported over long distance (Cohen, 1998).

Virtually complete removal of particles in the range of 0.1 to 10 μm in diameter is expected by wet deposition (Leuenberger *et al.*, 1985, Ligocki *et al.*, 1985 a,b). Since ETS particles are in this size range (0.1-1 μm), they are expected to be efficiently washed from the atmosphere by wet deposition. Wet deposition occurs due to events such as rain, cloud, fog, or snow.

C. NICOTINE

Nicotine is the principal alkaloid in tobacco and a major contributor to the addictive properties of tobacco. In ETS, studies report that nicotine is most commonly found in the gas phase within the environment (Eudy *et al.*, 1986; Thome *et al.*, 1986; Eatough *et al.*, 1986; Hammond *et al.*, 1987). Organic compounds with vapor pressure between 10^{-6} and 10 Pascals (Pa) at ambient temperatures are classified as semi-volatile organic compounds. At 298 °K, nicotine has a vapor pressure of 2.7 Pa and is almost entirely present in gas phase (Von Loy *et al.*, 2001). Less than five percent of ETS nicotine has been associated with the particulate phase (Jenkins *et al.*, 2000). Also, in sidestream smoke, the alkaline nature of ambient air leads to gas phase nicotine rather than in the particulate phase.

The semi-volatile constituent of ETS, such as nicotine, exhibit different atmospheric persistency depends on environmental conditions. In ambient air, nicotine may react with photochemically generated hydroxyl radicals and with ozone. The reported half-life of nicotine in the ambient atmosphere is approximately 1 day (Spectrum Chemical Fact Sheet, 2003).

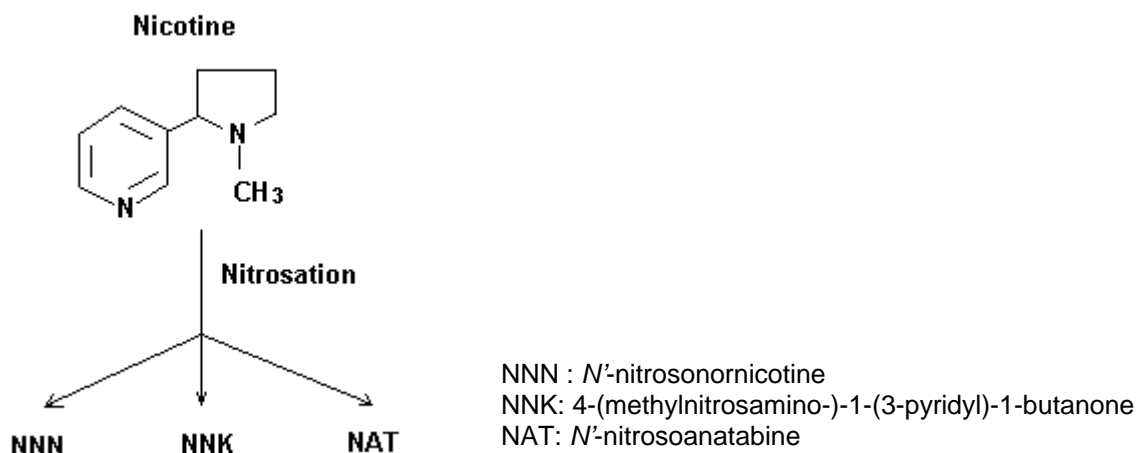
In indoor air, gas phase nicotine is rapidly diffuse to surrounding surfaces with which it interacts and expected to be removed from the environment at a faster rate than other ETS components (Eudy *et al.*, 1986; Eatough *et al.*, 1986). Studies show that the nicotine level decreases rapidly as consequence of sorptive uptake on different surrounding surfaces (Eatough *et al.*, 1986; Piade *et al.*, 1999; Von Loy *et al.*, 2001). Therefore, nicotine is a reasonable indicator of ETS exposures occurring within the previous few hours, with its indoor half-life of approximately two hours (Trinh and Huynh, 1989). Research also indicates that sorbed nicotine present on surrounding materials, such as walls and carpets, may be re-emitted to the environment over time (Trinh and Huynh, 1989). According to the Piade *et al.* (1999) study, as much as 1 mg of nicotine can be adsorbed and re-emitted from 1 m^2 of cotton cloth over a few hours. The Von Loy *et al.* (2001) chamber experiments also observed desorption of nicotine from surrounding materials. After flash evaporation of nicotine in a 20 m^3 environmental test chamber with a carpet floor covering (measured nicotine air concentration of 4.4 $\mu\text{g}/\text{m}^3$), the chamber was flushed with clean air for 3 days. After resealing the chamber, the nicotine concentration slowly rose back to 1 $\mu\text{g}/\text{m}^3$, which demonstrates the effect of nicotine being re-emitted from surrounding material surfaces.

D. TOBACCO-SPECIFIC N-NITROSAMINES

While nicotine has not been identified as a carcinogen, several tobacco-specific nitrosamines (TSNAs), which are derived from nicotine and other tobacco alkaloids, may be carcinogenic (Hecht and Hoffmann, 1988). TSNAs (see Figure VI-1) are formed by N-nitrosation of nicotine during the curing, processing, fermentation, and combustion of tobacco products (IARC 1986; Ashley *et al.*, 2003). The yield of TSNA from smoking depends on the nitrate content of tobacco. Certain flue-cured tobaccos exposed to NO_x during the curing process contain higher levels of TSNAs (Ashley *et al.*, 2003).

Figure VI-1

Nicotine Conversion



N'-nitrosornicotine (NNN) and 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) are believed to be the most potent carcinogens of the TSNA class (Ashley *et al.*, 2003).

N-nitroso compounds are degraded in the presence of ultraviolet and visible light. When heated to decomposition, these compounds emit toxic fumes of nitrogen oxides (NTP, 2002).

E. PAH AND PAH-DERIVATIVES

Researchers have identified at least ten polycyclic aromatic hydrocarbon (PAH) isomers in ETS, which have been identified as cancer causing toxic air contaminants (Hoffmann and Hoffmann, 1997; OEHHA, 1997). Some PAHs react with NO_x emissions in the atmosphere to mutate to form nitro-derivative PAHs (ARB, 1994). Both gas and particle phase PAHs have been measured in ETS (Gundel *et al.*, 1995). Table VI-2

shows a list of identified gaseous and particulate PAHs that have been identified in ETS.

Table VI-2
PAHs Detected in ETS

Gas-Phase PAHs	Particle-Phase PAHs
1-methylnaphthalene	1,2-benzofluorene
2-methylnaphthalene	Anthracene
Anthracene ^{1/}	Benz[a]anthracene
Benz[a]anthracene ^{1/}	Benzo[a]pyrene
Chrysene ^{1/}	Benzo[b]fluoranthene
Fluoranthene ^{1/}	Benzo[k]fluoranthene
Fluorene	Chrysene
Naphthalene	Fluoranthene
Phenanthrene	Phenanthrene
Pyrene ^{1/}	Pyrene
	Triphenylene

Source: Gundel *et al.*, 1995.

1/ PAHs are distributed between the gas and particle phases.

One of the most potent cancer-causing PAHs in ETS is benzo[a]pyrene. Benzo[a]pyrene exists almost entirely in the particle phase in the atmosphere with a size of three μm or less and, therefore, subject to wet and dry deposition (ARB, 1997b). The average half-life of particle benzo[a]pyrene in the atmosphere is estimated to be about 3.5 to 10 days and lifetime of 5 to 15 days (ARB, 1997b). Other lifetimes of PAHs are shown in Table VI-3.

Table VI-3
Estimated Atmospheric Lifetimes
of Selected PAHs

PAHs in ETS	Lifetime due to reaction with:		
	OH ^{a/}	NO ₃ ^{b/}	O ₃ ^{c/}
1- methylnaphthalene	3.5 hrs	50 days	>125 days
2-methylnaphthalene	3.6 hrs	40 days	>40 days
Anthracene	1.4 hrs		
Fluoranthene	~3.7 hrs ^{d/}	~85 days	
Pyrene	~3.7 hrs ^{d/}	~30 days	

Source: ARB, 1998.

a/ For a 12-hr daytime average OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn *et al.*, 1987).

b/ For a 12-hr average nighttime NO₃ radical concentration of 2.4×10^8 molecule cm^{-3} and an NO₂ concentration of 2.4×10^{12} molecule cm^{-3} (Atkinson *et al.*, 1986).

c/ For a 24 hr average O₃ concentration of 7×10^{11} molecule cm^{-3} (Logan, 1985).

d/ Using estimated OH radical reaction rate constant correlation with ionization potential (Biermann *et al.*, 1985; Arey *et al.*, 1990; Atkinson *et al.*, 1990).

Volatile, 2- to 4-ring PAHs exist in the atmosphere mostly in the gas phase (Atkinson and Arey, 1994). The gas-phase PAHs react with hydroxyl (OH) radicals, NO₃ radicals, and ozone in the atmosphere, with the OH radical reaction generally dominating as the PAHs loss process (Atkinson and Arey, 1994). The products of the OH radical reactions with PAHs include formation of hydroxyl-PAH, nitro-PAH, and ring-opened dicarbonyls (ARB, 1997b). The estimated half-life of the gas phase 2- and 4-ring volatile PAHs in the atmosphere due to reaction with the OH radical are in the range of 2 to 19 hours and have a lifetime of 3 to 27 hours, (Atkinson and Arey, 1994).

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