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# Seasonal variability of 1-chloropyrene on atmospheric particles and photostability in toluene

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#### Abstract

The occurrence of a mutagenic compound, 1-chloropyrene (Cl-Py), in extracts of ambient particulate matter at an urban site in Japan has been investigated. Samples were collected with a high-volume air sampler for 24h periods over the course of 1 week in winter (February), spring (May), summer (August), and autumn (November) 2002. The Cl-Py levels showed seasonal variation, ranging from  $2.4 \text{ pg/m}^3$  (summer) to  $18.9 \text{ pg/m}^3$  (winter). This variation would indicate that the lower temperatures in winter results in an increased distribution of Cl-Py from vapor phase to the particle phase. In addition, there is also the possibility that ambient Cl-Py is emitted from seasonal sources or is susceptible to photodegradation by sunlight, or both. The photodegradation of Cl-Py in a laboratory experiment was conducted to simulate the compound's fate on airborne particle surfaces. The degradation of Cl-Py proceeded by a first-order reaction with a rate constant of  $0.72 \text{ h}^{-1}$ . In the presence of a radical sensitizer, 9,10-anthraquinone (AQ), the photodegradation of Cl-Py (i.e., the formation of Py) occurred in the presence of AQ. (© 2004 Elsevier Ltd. All rights reserved.

Keywords: 1-Chloropyrene; Particulate matter; PAHs; Photodegradation; Radical sensitizer

### 1. Introduction

Organochlorine compounds as typified by polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have caused much concern, owing to their reproductive toxicity and carcinogenicity to humans (Fingerhut et al., 1991; IARC, 1997; US EPA, 1997). Their main source appears to be refuse incineration, and the compounds diffuse from incinerators into various environments (Alcock and Jones, 1996; Baker and Hites, 2000). The productions such PCDDs and PCDFs substantially make progress in the presence of organic compounds containing chlorine (Addink and Olie, 1995; Takasuga et al., 2000). Polycyclic aromatic hydrocarbons (PAHs) are also generated by the combustion of organic compounds and are known to be carcinogenic and mutagenic (Mastral and Callén, 2000; Richter and Howard, 2000; Boström et al., 2002). Considering the process by which those compounds are produced, chlorinated PAHs (Cl-PAHs) may also be produced concurrently with them. Yoshino and Urano (1997) have confirmed the presence of Cl-PAHs in exhaust gas from municipal waste incinerators. In addition, Weber et al. (2001) have reported a possible

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pathway for the formation of PCDFs from Cl-PAHs during incineration processes. With respect to the environmental distribution of Cl-PAHs, the presence of Cl-PAHs in tap water has been demonstrated (Shiraishi et al., 1985). The levels ranged from 0.1 to 0.01 ng/l for 10 species of Cl-PAHs, which Shiraishi et al. suggest were produced by the use of chlorine for the disinfection of public water supplies. However, little is known about the atmospheric behavior, fate, and potential degradation pathway of Cl-PAHs.

With respect to the mutagenicity of Cl-PAHs, Colmsjö et al. (1984) have reported that 1-chloropyrene (Cl-Py) shows an S9-dependent mutagenic effect in the *Salmonella* system, although pyrene, the parent compound, shows only weak mutagenicity. The increased mutagenicity of Cl-Py seems to be due to the epoxidation facilitated by introduction of chlorine into the molecule.

The main degradation pathway for PAHs and nitro-PAHs is driven by sunlight (Kamens et al., 1988; Fan et al., 1996). The photodegradation mechanisms have been investigated in laboratory experiments using chemical model systems as proxies for the organic phase of ambient aerosols (McDow et al., 1994; Jang and McDow, 1995; Feilberg and Nielsen, 2000; Feilberg and Nielsen, 2001). These studies indicate that photodegradation is likely to occur via an indirect pathway involving radical sensitizers such as polycyclic aromatic quinones.

In the current work, we investigated the occurrence of Cl-Py, a representative of the Cl-PAH group, in extracts of particles collected at an urban site in Shizuoka, Japan, and compared the observed levels with the PAH levels. We also studied the photostability of Cl-Py in chemical model systems both in the presence and in the absence of a photochemical radical sensitizer, 9,10anthraquinone (AQ).

#### 2. Experimental

### 2.1. Synthesis of 1-chloropyrene

Cl-Py was synthesized by the chlorination of pyrene (Py) (Wako Chemicals, Osaka, Japan) with *N*-chlorosuccinimide (NCS) (Wako Chemicals) following the procedure of Dewhurst and Kitchen (1972). A solution of NCS (2.0g) in 20ml propylene carbonate (PC) and a solution of Py (2.0g) in 20ml PC were mixed and allowed to react at 100 °C for 3h in the dark. The reaction solvent was fractionated by HPLC (Waters 515, Waters, Milford, MA) using a COSMOSIL 5C18-AR ( $20 \times 250$  mm; Nacalai Tesque, Inc., Kyoto, Japan) column and methanol as an eluent, and a flow rate of 10.0ml/min. The reaction products were detected by UV/VIS detector (Waters 2487) at the wavelength of 245 nm. The fraction corresponding to the dominant peak was isolated and analyzed by a Hewlett–Packard (HP) 6890 gas chromatography–HP 5972 A mass spectrometry (GC–MS) (Agilent Technologies, Palo Alto, CA, USA) and <sup>1</sup>H-NMR (JEOL JNM-GSX500 spectrometer). The analytical condition of GC–MS was showed in the section of Analytical procedure in detail. The mass spectrum of this compound contained a base peak at m/z = 236 (likely the molecular ion) and other prominent peaks at m/z = 200 (M-HCl), 118, and 100. The <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) peaks identified are as follows:  $\delta$ : 8.03–8.11 (m, 5H), 8.19–8.24 (m, 3H), 8.48 (d, 1H). On the basis of these analytical results, the isolated product was identified as Cl-Py. GC–MS indicated a purity of >95% (by area).

#### 2.2. Sampling procedure

Monitoring was conducted at a rooftop location (20m above ground level) on the University of Shizuoka campus (lat 34°59' N, long 138°27' E) situated  $\approx 1 \text{ km}$ from the nearest busy road and  $\approx 6 \text{ km}$  from the city center. Particulate matter was collected on glass fiber filters  $(20.3 \times 25.4 \text{ cm}; \text{Type A/E Gelman Sciences Inc., Ann}$ Arbor, MI, USA) by a high-volume air sampler (SIBA-TA Scientific Technology Ltd., Tokyo, Japan). The sampler operated at a constant flow rate of  $\approx 1.0 \,\mathrm{m^3/min}$ . Samples were collected over a period of 24h, yielding sampled air volumes of  $\approx 1440 \,\mathrm{m^3}$ , for 7 consecutive days during 4 months: February (winter), May (spring), August (summer), and November (autumn) 2002. The seasonal concentrations were calculated from the total of the 7 days for each season. After the samples were taken, the filters were wrapped in aluminum foil and stored in a freezer at -45°C until they were extracted.

#### 2.3. Extraction and clean-up

During the entire treatment procedure, the samples were protected from light to avoid photochemical degradation of the analytes. The filters were extracted ultrasonically with 50.0 ml of dichloromethane containing phenanthrene- $d_{10}$  (63 ng) and perylene- $d_{12}$  (155 ng) as internal standards. The extraction lasted 20min. After centrifugal separation (10min, 3000rpm), 40ml of the supernatant fluid solution was used as the sample solution. It was concentrated to  $\approx 5 \text{ ml}$  in a rotary evaporator and then blown down to  $\approx 1 \text{ ml}$  under a gentle stream of  $N_2$  through an XAD-2 resin to trap impurities at 30 °C. The concentrated solution was cleaned up by means of a glass solid-phase extraction tube (SUPELCO, Inc., Bellefonte, PA, USA) packed with silica (500 mg; particle size, 40 µm; SUPELCO), which was eluted with 10ml mixed solvent of n-hexane and dichloromethane (9:1 v:v). The eluate was concentrated to  $\approx 300 \,\mu$ l under a gentle stream of N<sub>2</sub> at 30°C for GC-MS analysis.

Particulate PAHs were extracted with dichloromethane. PAHs were also extracted in an ultrasonic bath for 20 min. After centrifugation at 3000 rpm for 10 min, a known volume of extract was transferred to another test tube. DMSO ( $50 \mu$ l) was then added to preserve the PAHs, and the solvent was evaporated under N<sub>2</sub>. The residues were then dissolved in 950 µl of acetonitrile, and the target PAHs were separated by HPLC.

## 2.4. Analytical procedure

Analysis of Cl-Py was performed on a HP 6890 GC– HP 5972A MS system. The capillary column was a DB-5 (5% phenyl-methylpolysiloxane,  $60 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$ , J&W Scientific). Helium was used as a carrier gas at a flow rate of 1.0 ml/min. The oven temperature was kept at 80 °C for 2 min, then increased from 80 °C to 300 °C at a rate of 5 °C/min, and then kept 300 °C for 20 min. The temperature of the injector and GC– MS transfer line was kept at 300 °C. The MS detector was run in electron impact ionization mode, and the electron energy was 70 eV. Qualification of Cl-Py was performed in selected-ion monitoring mode using the molecular ions 236 and 238.

The PAHs were separated on an HPLC system consisting of an L-6000 series pump, an L-5090 degasser, an AS-2000 autosampler, an F-1080 spectrofluorometer (Hitachi Corp., Tokyo, Japan), a mixer (Agilent Technologies), a CO630 column oven, and a six-way valve (GL Science Corp., Tokyo, Japan). The precolumn  $(4.6-mm i.d. \times 30 mm)$  for PAH condensation and clean-up and the main column (4.6-mm i.d.  $\times$  250 mm) for PAH separation were Wakosil-II 5C-18 PAH (Wako Chemicals). PAHs were detected by two spectrofluorometers connected in series, with detection wavelengths automatically changing during analysis. The HPLC analytical conditions have been described elsewhere (Ohura et al., 2002; Ohura et al., 2004). The following PAHs were monitored: pyrene (Py), benz[a]anthracene (BaA), benzo[a]pyrene (BaP), and benzo[ghi]perylene (BghiP).

The recovery test was carried out the addition of Cl-Py solution (1.4 ng) as the spike to the collected filter samples, followed by the extraction and analysis as described in above.

#### 2.5. Photodegradation experiments

Photodegradation experiments were performed with a turntable photoreactor using a 450-W high-pressure mercury lamp (USHIO Co., Ltd., Tokyo, Japan) as the light source. The lamp was placed in a quartz immersion well with cooling water. The immersion well was surrounded by a Pyrex sleeve to filter out high-energy UV bands ( $\lambda > 290$  nm). Although this setup does not resemble the spectral distribution of the actinic flux, it does reproduce the wavelengths normally encountered in the atmosphere. The photoreactor was positioned in a water bath with constant water circulation. The temperature in the water bath was maintained at  $25 \pm 1$  °C. The solutions were irradiated in  $13 \times 100$  mm quartz reaction tubes.

The synthesized Cl-Py was dissolved in toluene at a concentration of  $\sim 0.15$  mM. Samples were removed with a pipette and transferred to brown chromatography vials. The samples were analyzed for identification of the photolysis products using the GC–MS condition as showed in section of Analytical procedure, but in scan mode. Experiments were carried out both in pure solution and in the presence of AQ as a radical sensitizer.

#### 3. Results and discussion

#### 3.1. Concentration of Cl-Py

The detection limit for Cl-Py for our method was defined as 3 times the standard deviation of the peak area of a dilute standard solution, which was established as  $0.72 \text{ pg/m}^3$  in terms of ambient concentration. When laboratory blanks were analyzed by the established method, Cl-Py was not detected. Recovery tests of Cl-Py from particles were 91 ± 14%. Reproducibility tests indicated that the coefficient of variation of Cl-Py concentrations was less than 26%.

Ambient particle samples from the four seasons were extracted and analyzed for Cl-Py. Cl-Py was detected in all the samples, indicating its ubiquitous distribution. The ambient levels ranged from 2.4 (summer) to 18.9 (winter) pg/m<sup>3</sup> (Fig. 1). The levels observed in spring and autumn were 2.6 and 4.4 pg/m<sup>3</sup>, respectively. The mean value for the four seasons was 7.1 pg/m<sup>3</sup>, which was somewhat higher than the values for particle samples collected from an urban street, 4.9 pg/m<sup>3</sup> (Nilsson and Östman, 1993). The concentrations of Cl-Py associated with particles were higher in winter and autumn than in summer and spring. Similar trends for PAHs associated with particles were also observed in this study (Fig. 1). In addition, we observed significant correlation over the seasons between the concentrations of Cl-Py and Py associated with particles (p < 0.01) (data not shown). These facts indicate that the behavior of Cl-Py in air may be similar to that of the parent compound, Py, although their concentration levels differ considerably. The ratio of the maximum value to the minimum value (the concentration ratio of winter/summer) for Cl-Py was 7.9, although the ratios for the PAHs ranged from 2.0 to 5.9. The larger variability of the Cl-Py concentration may indicate that the lower temperatures in winter results in an increased distribution of Cl-Py from vapor phase to the particle phase as shown in the case of ambient PAHs (Ohura et al., 2002; Ohura et al., 2004). In addition, there is also the possibility that the ambient



Fig. 1. Comparison of the Cl-Py and PAH levels for each sampling season.

Cl-Py levels were strongly dominated by the possible seasonal sources, or by photochemical degradation during periods of high solar radiation. On the other hand, secondary reactions in air may be another source of Cl-Py because it is formed easily by the photochemical chlorination of pyrene (Nilsson and Colmsjö, 1989, 1990). Nilsson and Ostman (1993) suggest that automobile traffic may be a major source of Cl-PAHs in the street environment, because the concentration profiles of Cl-PAH in street and road tunnel samples were similar. Municipal waste incineration plants, a major source of atmospheric PCDDs/PCDFs, may also be a source of Cl-PAH. It is therefore difficult to determine the importance of the various sources; further investigation will be needed to clarify the behavior and occurrence of Cl-PAH species.

### 3.2. Photostability of Cl-Py

In order to clarify the photostability of Cl-Py, we simulated the photodecay in laboratory experiments using chemical model systems. Fig. 2 shows the time dependence of the decay of Cl-Py and Py in toluene during the irradiation. Decay of Cl-Py and Py apparently can be described by first-order kinetics, and Py was more stable than Cl-Py during the course of the experiment. This result indicates that the addition of a chlorine atom to Py accelerated the photodecay. The rate constants, linear regression coefficients  $(R^2)$ , and half-lives for the degradation of Cl-Py, Py, and 1-nitropyrene (1NP) are compared in Table 1. The rate constant for the degradation of Cl-Py was significantly smaller than that of 1NP, which has been suggested to be emitted directly from vehicles and distributed ubiquitously in air (Feilberg et al., 2001). Hayakawa et al. (1995) detected ambient 1NP levels that were nearly 3 orders of magnitude higher than the levels of Cl-Py we observed in this study. The



Fig. 2. Photostability of Cl-Py (in the presence and absence of AQ) and Py in toluene, expressed as  $\ln(C/C_0)$  vs. time. The solid lines are linear regressions of the data.

First-order decay rate constants and half-lives of Py derivative	Table 1	
	First-order decay rate constants and half-lives of Py deriv	atives

Compound	$k (h^{-1})$	$R^2$	$t_{1/2}$ (h)	
Ру	0.44	0.914	1.58	
1NP	15	0.945	0.05	
Cl-Py	0.72	0.976	0.96	
Cl-Py + AQ	1.38	0.991	0.50	

low atmospheric levels of Cl-Py that we measured cannot be explained by the photodegradation and must therefore have been caused by low emission rates.

With regard to the direct photolysis of PCDDs/ PCDFs, as chlorinated aromatic compounds that can undergo reductive dechlorination followed by further reaction steps, the extent of dechlorination has occurred in less than 20% (Kim and O'Keefe, 2000). In the case of photolysis of Cl-Py, we observed no pyrene produced by reductive dechlorination during the irradiation. In addition, we did not find significant photolysis products resulting from Py irradiation. These results suggest that C-Py undergoes fragmentation immediately upon irradiation. Also, Kim and O'Keefe (2000) reported that dechlorination of PCDD/Fs was accelerated by the use of solvents with greater hydrogen-donor potential when photolysis was carried out by means of this technique. Therefore, the nature of the solvent (i.e., aerosol organic composition) will play an important role in the photolysis of the compounds associated with particles.

#### 3.3. Influence of a radical sensitizer

Reactive oxy-PAHs with an  $(n\pi^*)$  triplet state configuration are known to efficiently abstract hydrogen from donors, and hydrogen abstraction is followed by further reaction (Eqs. (1) and (2), where ArCO denotes an oxy-PAH) (Feilberg and Nielsen, 2000).

$$ArCO + hv \to {}^{1}ArCO^{*} \to {}^{3}ArCO^{*}$$
(1)

$${}^{3}\text{ArCO}^{*} + \text{RH} \rightarrow \text{ArCOH}^{\bullet} + \text{R}^{\bullet}$$
  
 $\rightarrow$  radical chain reactions (2)

The radical synthesizer anthraquinone (AQ) was found to strongly accelerate the photodegradation of nitro-PAHs as well as PAHs in an organic medium (Jang and McDow, 1995; Feilberg and Nielsen, 2000; Feilberg and Nielsen, 2001; Feilberg et al., 2002). In addition, AQ is present in ambient particulate matter  $(4.1 \pm 1.6 \text{ ng/m}^3)$  (Rogge et al., 1993) and traffic soot (4.4-24.3 µg/km) (Nielsen et al., 1999). In previous study, we found that the photolysis rate of 3-nitrobenzanthrone (<0.1 mM) using the photoreactor became a maximum when 5.0 mM AQ was added to the solvent (Feilberg et al., 2002). As a part of this study, we irradiated Cl-Py in toluene in the presence of AQ (5.0mM). The photolysis proceeded by a first-order reaction (Fig. 2). The rate constant in the presence of AQ was about two times as high as that in the absence of AQ (Table 1), which indicates that addition of a radical sensitizer affects the photolysis rate of Cl-Py. This result suggests the possibility that a radical chain reaction initiated through hydrogen abstraction from the solvent by AQ could be responsible for Cl-Py decay. Here, it is interesting to note that small amounts of Py, formed by dechlorination of Cl-Py, were observed to build up over time (Fig. 3). The relation between the decay of Cl-Py and the formation of Py showed significant correlation  $(R^2 = 0.956, p < 0.01)$ , which indicates that the reaction steps from the excited state Cl-Py to Py proceeded rapidly (insert, Fig. 3). Because toluene is a



strong hydrogen donor, Cl-Py dechlorinated by the irradiation would be expected to accept hydrogen abstracted from toluene by excited state triplet AQ, resulting in the formation of Py.

## 3.4. Radical formation

For the decay process in actual environments, radical reactions are important and perhaps dominating. The possibility of radical formation under the experiment conditions can be revealed from the identification of the hydrogen abstraction compounds of the solvent. That is, formation of bibenzyl (1,2-diphenylethane) can be used as an indicator because bibenzyl is a byproduct of hydrogen abstraction from toluene (Jang and McDow, 1995). In Fig. 4, the ratio of integrated bibenzyl area to internal standard area (i.e., relative bibenzyl concentration) is plotted against irradiation time of Cl-Py in the presence (5mM) and absence of AQ. Bibenzyl was not analyzed in the first experiment. The rates of bibenzyl formation in the presence and absence of AQ were considerably different, which indicates that AQ readily abstracted hydrogen from toluene. These facts support our hypothesis about the production mechanism of Py as a photolysis product in the presence of AQ. In addition, the variation in bibenzyl formation rates in the presence and absence of AQ is significantly greater than the variation in the corresponding Cl-Py decay rates. This fact may be due to the complex nature of the degradation mechanism and to the indirect effect of AQ, which has an "inner filter" (light-absorbing) effect (Feilberg et al., 2002).





Fig. 4. Bibenzyl production from Cl-Py in the presence and absence of AQ.

The photodegradation processes of aerosol organic compounds such as PAHs are known to depend on the hydrogen-donating abilities of the organic components and on singlet oxygen solubility in the aerosol particle. Thus the model studies in this work appeared to describe the possible photodegradation reaction mechanisms of Cl-Py in organic aerosols.

## 4. Conclusions

Mutagenic Cl-Py was detected in particles from urban air at levels ranging from 2.4 to  $18.9 \text{ pg/m}^3$ . The levels were  $\approx 1/30$  to 1/130 times those of the parent compound, Py. The Cl-Py levels showed greater seasonal variability than the corresponding PAH levels. Thus, the concentration of Cl-Py associated with particle may be affected by not only the distribution of gas/particle phase for seasons but also seasonal sources such as space heating or photodegradability by sunlight, or both. With respect to the formation of Cl-Py in the air, the secondary reaction by long-range transport may be also expected because of high reactivity of Cl-Py.

The photostability of Cl-Py was investigated in an organic solvent that simulates airborne particle surfaces. The decay exhibited first-order kinetics, and the rate constant was greater than that of Py, the parent compound. Addition of a radical sensitizer, AQ, accelerated the photolysis of Cl-Py. The mechanism of the formation of the photolysis products of Cl-Py during irradiation was different in the presence of AQ than in the absence of AQ. In the former case, the dechlorination of Cl-Py would proceed by hydrogen abstraction from the solvent by AQ.

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