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IDENTIFICATION AND CHARACTERIZATION OF 4-PHENYLCYCLOHEXENE- AN EMISSION PRODUCT FROM NEW CARPETING

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4-Phenylcyclohexene
An Indoor Air Pollutant
Emitted by Certain Batches of New Carpet

Introduction

Indoor air pollution represents an area of increasing concern due to a multitude of health complaints expressed by homeowners and business proprietors regarding the quality of their indoor environments. Such indoor air pollution problems, collectively known as the "tight building syndrome," actually result from a combination of factors including, 1) energy efficient buildings which tend to concentrate contaminants, particularly when no fresh-or make-up air is continuously added to recirculated indoor room air, and 2) the introduction or accumulation of an often unidentified chemical or biological contaminant. Frequently, there appears to be an association between the onset of health complaints and an individual's contact with a renovated or new environment such as a home or office workplace. In certain instances, however, health episodes have developed in environments previously considered "healthful."

As shown in Figure 1, indoor air, once considered cleaner than outside air, is now considered more contaminated. Although a variety of low level contaminants exist, few have been directly associated with ill health or the onset of health problems. To complicate the matter, many symptoms experienced by individuals are not definitive, and include complaints such as headache, sleeplessness, lethargy, and the onset or aggravation of upper respiratory problems. Yet, the development of subtle symptomatology following the introduction of certain pollutant sources or the cessation of those symptoms following the removal of suspect sources implicates specific chemical emissions in causation of various health problems. For example, low levels of formaldehyde gas often have been found to be a frequent offender. Sources of this specific contaminant have included urea-formaldehyde foam insulation (UFFI), particle board, other formaldehyde-resin based materials and, in the past, new carpet.

With regard to carpet emissions, in the last several years various health and related agencies in Arizona and nation-wide (i.e, CPSC) have received numerous calls expressing health concerns following the installation of new carpeting. Symptoms reported by "affected" individuals include those listed in Table 1. Monitoring of these environments, however, have revealed acceptable levels of formaldehyde gas (i.e., less than 30 ppb). These findings demonstrating acceptable levels of formaldehyde gas are consistent with industry reports that formaldehyde-emitting materials have been eliminated from new carpet. In most cases investigated in Tucson, however, the characteristic new carpet odor inside the home or office workplace, was quite pungent and, in certain instances, had resulted in the closing of entire buildings. In one case, for example, several hundred personnel were given leave for one day from a governmental facility following the installation of new carpeting. Further, numerous employees at the local Social Security office also experienced distinctive health effects such as nausea, vomiting, headaches and respiratory problems following installation of an indoor-outdoor type of carpeting. Many homeowners as well have experienced health problems following the installation of new carpet. These problems persist until there has been a significant reduction in the magnitude of the new carpet odor within the home. It has been of interest, therefore, to investigate the chemical nature of the emission product(s) from new carpet.

Initial Assessments of Emission Products

Research by Crabb (1984) at the University of Arizona revealed a predominant common emission product from three different carpet samples collected from "affected" environments. Headspace analysis of these carpet samples using a GC/Mass Spectrometer revealed the presence of a common contaminant, 4-phenylcyclohexene (4-PC) (see Table 2). Review of the literature indicated that production of styrene-butadiene rubber (SBR) latex adhesive could result in the formation of 4-phenylcyclohexene, a manufacturing by-product, as shown in Figure 2. SBR latex is frequently employed to bind the backing of the carpet to the weave as illustrated in Figure 3.

Miksch et al (1982) in their assessments of indoor environments identified a variety of indoor air contaminants including 3-phenylcyclohexene[1]. (See Table 3) The authors suspected the source of this particular indoor air contaminant to be carpeting, although they did not associate this chemical with the odor of new carpet nor did they suspect it as a potential contributor to indoor health problems.

Preliminary Environmental Assessments

Due to the commercial unavailability of 4-phenylcyclohexene, initial environmental studies to assess airborne levels of 4-PC relied upon quantification using 1-phenylcyclohexene (Figure 4), an isomer of 4-PC. To facilitate more detailed environmental assessments, however, it was necessary to

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[1]Difficulties with the nomenclature of this family of compounds suggest that the 3-phenylcyclohexene reported by Miksch et al (1982) was probably 4-PC.

synthesize 4-phenylcyclohexene. Interestingly, the final 4-PC product was a clear liquid, possessing the odor or essence of new carpet.

Monitoring of indoor environments following the installation of new carpeting was undertaken next to determine indoor levels of this chemical. Preliminary sampling of a variety of environments (homes, apartments, etc.) demonstrated 4-PC levels between 0.3 ppb and 20 ppb, the later concentration presenting a rather pungent odor to the investigators. As demonstrated in Figure 5, 4-PC levels in test apartments ranged from <0.3 ppb prior to installation to approximately 10 ppb 4 days after installation. The limited environmental data collected to date do suggest that 4-PC levels decay over time; after a period of about 2 months, levels decrease to approximately 1 to 2 ppb (see Figure 6). The odor threshold appears to be below 0.5 ppb.

<u>Initial Toxicological Testing</u>

Acute Oral Toxicity

Since a review of the literature did not reveal toxicological information on 4-PC, a battery of preliminary tests were initiated to obtain some appreciation of the toxic effects of this chemical. Preliminary studies evaluating the acute oral toxicity of 4-PC indicate that the LD_{50} for Sprague-Dawley Rats was between 500 and 5000 mg/kg. To be specific, three of five test animals dosed with 5000 mg/kg were terminated in moribund condition after one day, the remainder in two days. Prior to termination, the animals experienced tremors, spasms and oral secretions around the mouth and nose.

Necropsy observations on animals terminated on day 1 revealed that the small intestines of all animals were filled with solid yellow material and the stomach was bloated; hemorrhagic lungs and livers were noted in two animals.

The 500 mg/kg dosed rats demonstrated little outward adverse reaction to the 4-PC. The only observed effect was slight lethargy experienced about 10 minutes after dosing. No difference in heart-lung weights were noted between test animals and controls. Large polyps were noted on the small intestine of 4 of the 5 test animals. The polyps were ultimately identified as enlarged lymphoid follicles. Slight hemorrhaging and enlargement of the heart occurred in two animals. Darkening of the liver was noted in another animal.

Skin Irritancy

Skin irritancy of 4-PC was evaluated by applying 0.1ml of the chemical to one inch square patches of abraded and unabraded skin of six Hartley guinea pigs for a 24-hour period. The testing revealed that 4-PC is not a positive irritant (score of 0.25; score of 5 required).

Eye Irritancy

The potential for 4-PC to induce eye irritation was also evaluated by introducing 0.1ml of 4-PC into the eyes of six albino New Zealand rabbits. Eye reactions were graded at 24, 48 & 72 hours post exposure. 4-PC was not determined to be a positive eye irritant (i.e., cornea, iris and conjunctivae were generally normal), although slight reddening and swelling of the eyelid did occur in one animal. Upon dosing, rabbits did not squeal; all animals intermittently rubbed their eyes and kept them closed over the duration of the exposure. Two drops of Opthetic (proparacaine HCL) 0.5% analgesic was added 10-15 minutes after dosing to relieve apparent discomfort characterized by the rabbits' rubbing of eyes and continued eye-closing.

Pulmonary Response

Since many individuals exposed to 4-PC following carpet installation experience respiratory problems, it was of further interest to develop some appreciation of the pulmonary response to the chemical. The irritancy of the 4-PC to pulmonary tissue, was evaluated by instilling 2ul of 4-PC into the surgically exposed trachea of 4 rats. At the end of 15 days, the animals were terminated and necropsied. Hemorrhaging within the lungs of 2 of the 4-phenylcyclohexene-dosed rats was evident, impacting primarily the bronchioles. LDH (lactate dehydrogenase) from lung lavage was also elevated, approximately 400%, suggesting cellular damage (cell permeability and lysis) to pulmonary tissue.

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1. Crabbe, Cynthia L. 1984. Odorous Emissions from New Carpeting: Development of Field-Monitoring and Analytical Technique. Masters Thesis, Department of Pharmacology and Toxicology, University of Arizona, Tucson, Arizona.

2. Miksch, R.R., C.D. Hollowell, and H.E. Schmidt. 1982. Trace Organic Chemical Contaminants in Office Spaces. Environ. Int. 8: 129-137.

3. Shoskes, L. 1974. Contract Carpeting. New York: Watson-Guptill Publications.

4. Walsh, Dale W. 1986. Preliminary Evaluation of the Environmental Concentration and Toxicity of 4-phenylcyclohexene: An Emission of New Carpeting. Masters Thesis, Department of Pharmacology and Toxicology, University of Arizona, Tucson, Arizona.

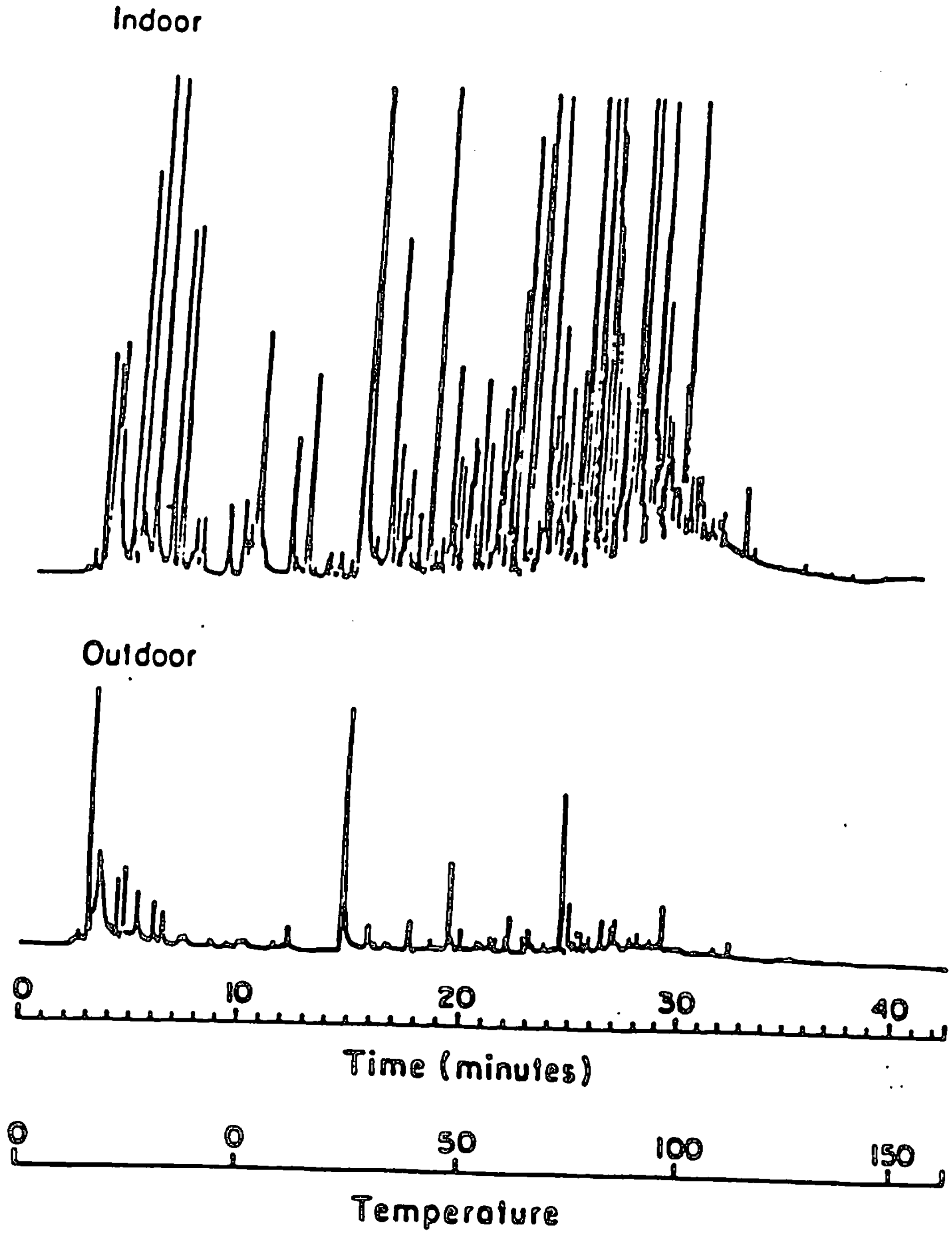


Figure 1. Gas Chromatographs of Indoor and Outdoor Air Samples Comparing Number of Contaminants Found In Each Environment

From Miksch, Hollowell and Schmidt 1982.

Table 1. Symptoms Reported After New Carpet Installation.

Person	Area	Symptoms
A.S.	Residence	Eye irritation, headache, lethargy, nausea
K.M.	Office Bldg.	Belligerence, lip and tongue stinging headache, worsening of arthritic condition
S.S.	Office Bldg.	Headache, sinus pressure, burning of eyes, decreased focusing ability
S.R.	Office Bldg.	Tearing and burning of eyes, headache
A.C.	Office Bldg.	Sinus pressure, burning of eyes
L.N.	Office Bldg.	Light-headedness, burning of eyes
Mgr.	Office Bldg.	Headache, burning of eyes

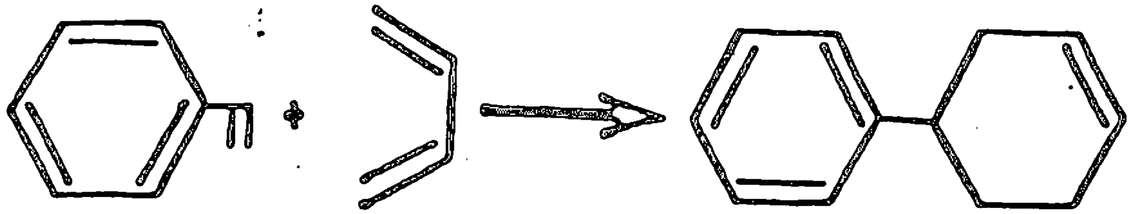
From Crabbe 1984.

Table 2. Compounds Identified in Carpet Samples by GC-MS.

Blue Carpet	Brown Carpet	Toluene Extracted Brown Carpet
4PC[a]	4PC[a]	4PC[a]
Dimethyl benzene	Low molecular weight hydrocarbon (C_9H_{15})	Low molecular weight hydrocarbon (C_8H_{16})
Propyl benzene	Low molecular weight hydrocarbon ($C_{12}H_{24}$)	Butylated hydroxy-toluene (BHT)
Low molecular weight hydrocarbon (C_9H_{12})		Unidentified compound (possibly a low molecular weight amide from the carpet fiber)

[a]4PC refers to 4-phenylcyclohexene which was identified as 1-phenyl-3-cyclohexene by Crabbe (1984).

From Crabbe 1984.



Styrene | 1,3-Butadiene | 4-Phenylcyclohexene

Figure 2. Diels-Alder Reaction of Styrene and 1,3-Butadiene to Produce 4-Phenylcyclohexene

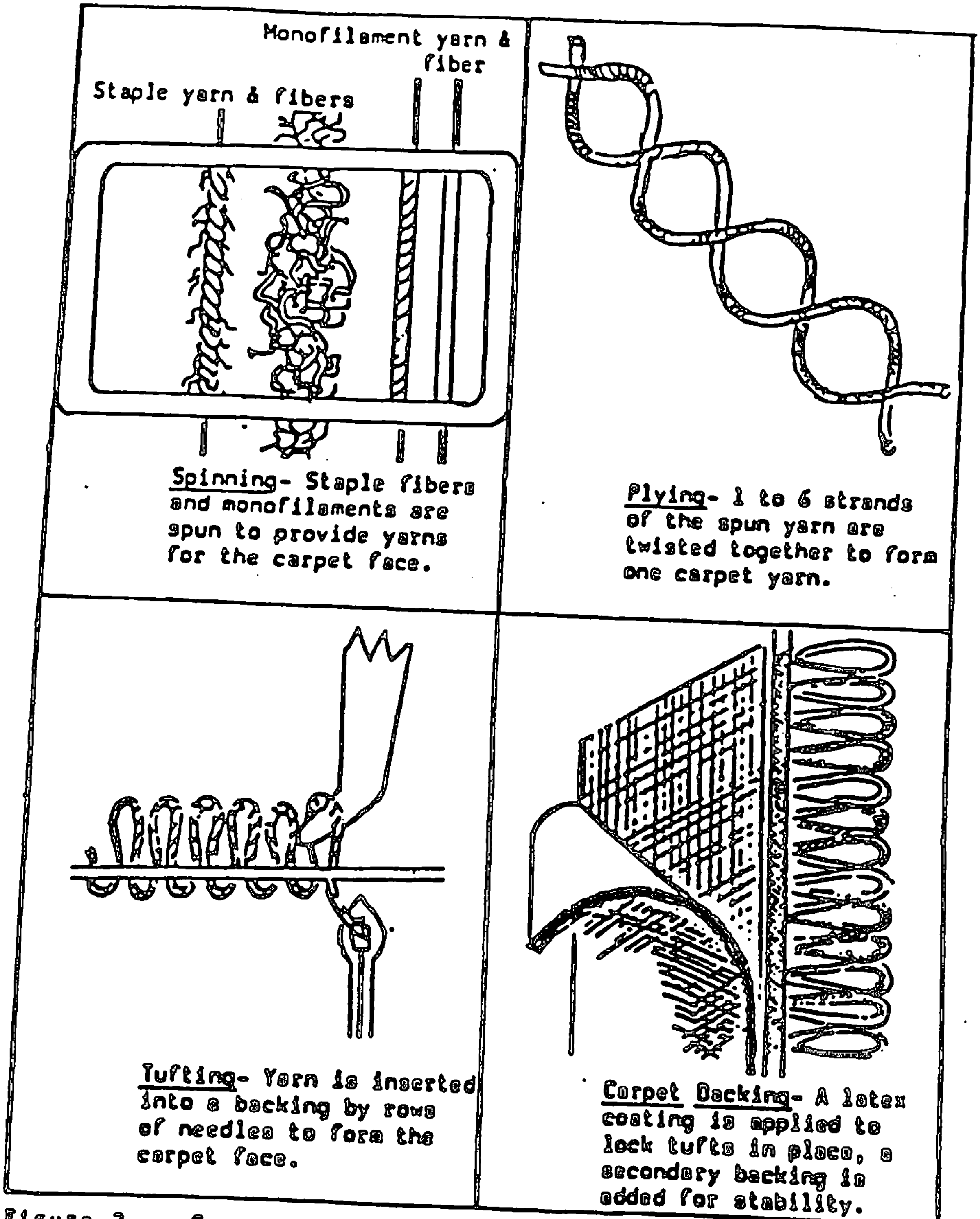


Figure 3. Construction of Carpets: Spinning, Plying, Tufting and Carpet Backing.

Derived from Shoakes 1976.

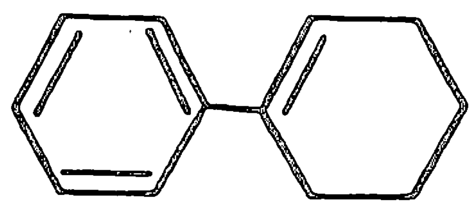
Table 3. Organic Contaminants Identified in Headspace Vapor Over Selected Carpet Samples.

Carpet Number	Description	Major[a] Organic Contaminants
1	nylon(?) fiber, jute backing	3-phenylcyclohexene[b], aliphatic hydrocarbons
2	polypropylene fiber, foam backing, self-stick	trimethylcyclohexene, aliphatic hydrocarbons
3	synthetic fiber, thin composition backing	n-octane, n-nonane, aliphatic hydrocarbons
4	nylon fiber, jute backing	3-phenylcyclohexene[b], decane, dichlorobenzene[b], styrene[b], aliphatic hydrocarbons
5	acrylic fiber, foam backing	heavy oxygenated compound[b], aliphatic hydrocarbons

[a]"Major" is defined as one of the five largest gas chromatographic peaks observed.

[b]Compounds which possess functional groups which enhance chemical reactivity.

Adapted from Miksch, Hollowell and Schmidt 1982.



1-Phenylcyclohexene

Figure 6. Structure of 1-Phenylcyclohexene Which Serves as the Internal Standard in the Gas Chromatographic Technique.

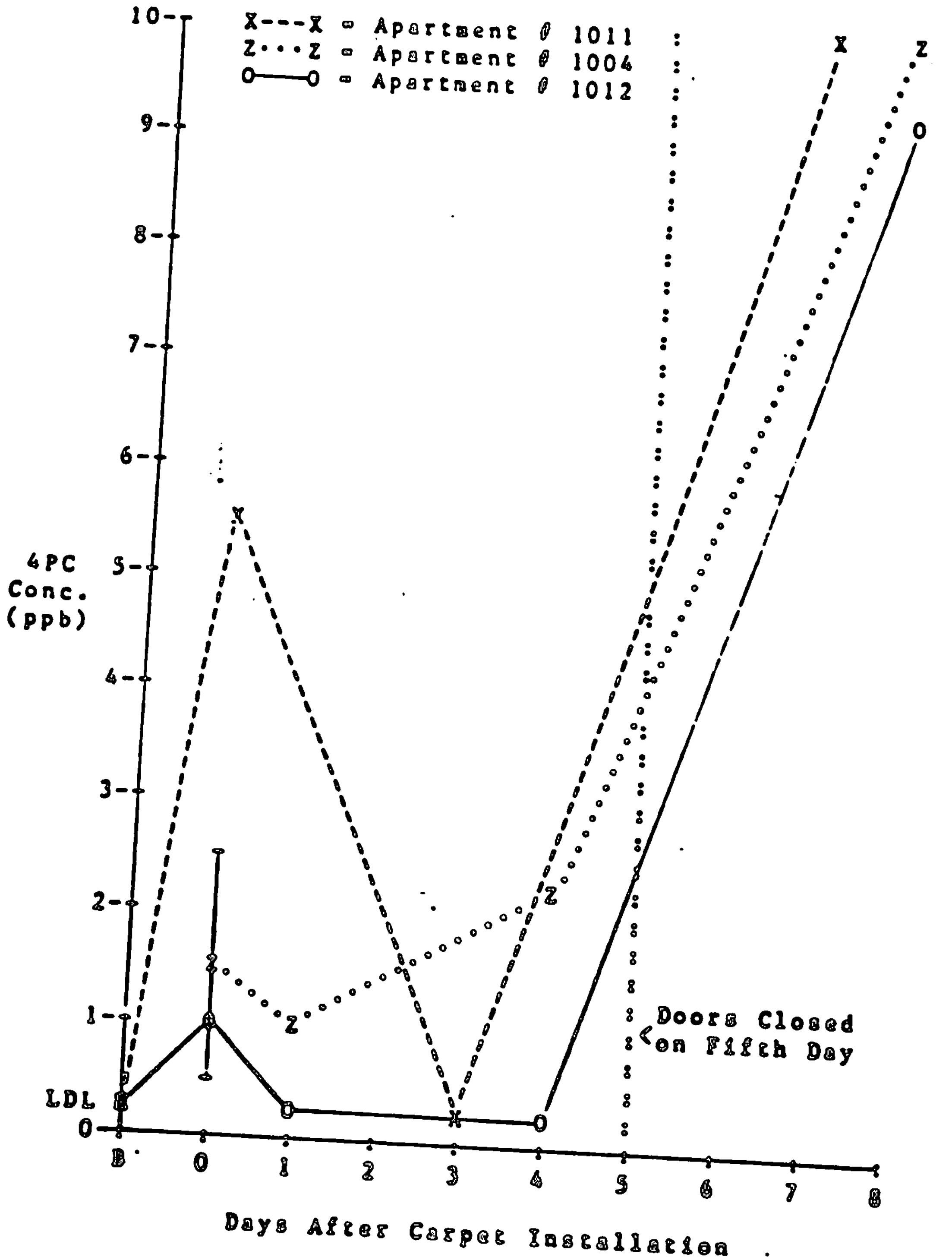


Figure 5. Variation in the Air Concentration of 4PC Over Time at P.F.W. Apartments.

LDL = Lower Detectable Limit

B = Before Installation

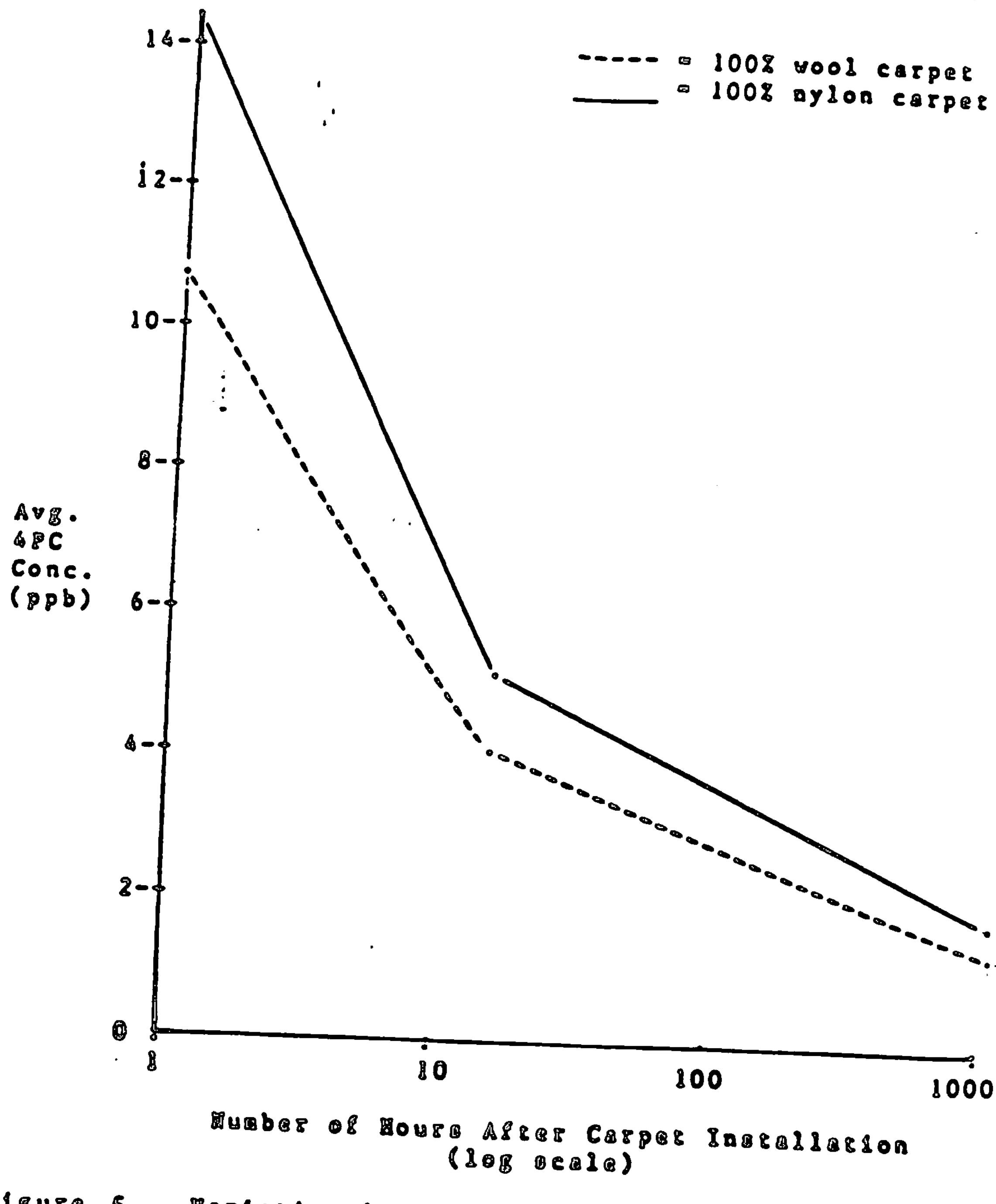


Figure 6. Variation in Average Environmental 4PC Concentrations of 100% Wool and 100% Nylon Carpets Over Time at T.R., Residence.

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exemptions allowing unregistered pesticide uses published (52 FR 45238, Nov. 25) . . . State Dept. and EPA to prepare "legislation EIS" on possible protocol for protection of ozone layer (52 FR 45520, Nov. 30) . . . Final rule revises regs implementing 1984 Hazardous and Solid Waste Amendments (52 FR 45788, Dec. 1) . . . State allotments for 1987 municipal wastewater facility grants published (52 FR 45860, Dec. 2) . . . Special local need pesticide registrations from 30 states published (52 FR 45863, Dec. 2).

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Jackie —

ARIZONA: TOXIC OFFGASSING FROM CARPETS?

Toxicologists at the University of Arizona believe that 4-phenylcyclohexene, the chemical that gives new carpets their characteristic odor, is making people sick. Numerous complaints over the past few years of headaches, upper-respiratory irritation, and even vomiting, from occupants of buildings with new carpeting, led the University's Toxicology Department to embark on a 3-year study of the problem. They identified the chemical--which is found in small amounts in the latex backing of new carpets, synthesized it, and after finding that virtually no literature on the substance exists, tested it on their own laboratory rats. A combination of intratracheal and feeding studies showed the chemical to cause hemorrhaging in the lungs and lesions and polyps in the intestines. The lead researcher on the study, Dr. Marc Van Ert--who hopes to do further work on the chemical--says the results of the study will be published soon. Contact: Dr. Van Ert, 602/626-4249. is sending FYI to DCO.

CONNECTICUT: RADON LEVELS SURVEYED

Connecticut is preparing to announce the results of a 2-year survey that sought to link indoor air radon levels with geologic, hydrologic, and household parameters. The study, done jointly by the state's Department of Health Services and Department of Environmental Protection, sampled private bedrock well water and indoor air in more than 200 homes throughout the state. As expected, the researchers found a clear association between each of the three parameters and indoor air radon levels. The lowest water and air levels were found in homes over sedimentary formations; the highest levels in both were associated with granite. Indoor air levels were also clearly associated with levels in water, though less than 20% of indoor air radon is thought to have water as its source. Other findings: the deeper the overburden (soil above the bedrock), the higher the radon levels in well water; type of house foundation, e.g., highly porous cinder block, is strongly associated with indoor radon levels; and--contrary to expectation--energy-efficient homes often have lower indoor air radon levels, perhaps because they tend to be newer and have fewer foundation cracks. The survey found the highest radon levels in the northeast region of the state, the lowest in the central valley. The range of air values found was 0.1-24.6 picocuries/liter, with the geometric mean at 1.26; 89% of the homes were below the EPA action guideline level of 4 picocuries/liter. Contact: Lynne Rothney, DHS, 203/566-8167.