A PRIMER ON INDOOR AIR QUALITY; TESTING, FORMULATIONS, SOLVENTS AND SUBSTRATES

Dan Pourreau, Ph.D.
Lyondell Chemical Company, a LyondellBasell Company
Thinking Green in the Bluegrass - June 26th, 2008
Churchill Downs, Louisville, KY

Outline

- **Indoor vs. Outdoor Air Pollutants**
- **What are VOCs?**
- **Indoor Air Quality concerns: are they legitimate?**
- **Regulations and Paint Certification Initiatives**
- **EPA Capstone report**
  - **Emissions from alkyd paints**
  - **Emissions from conventional latex paint**
  - **Emissions from low-VOC paints**
- **Emissions from low-VOC TBAC-based paints**
- **Conclusions**

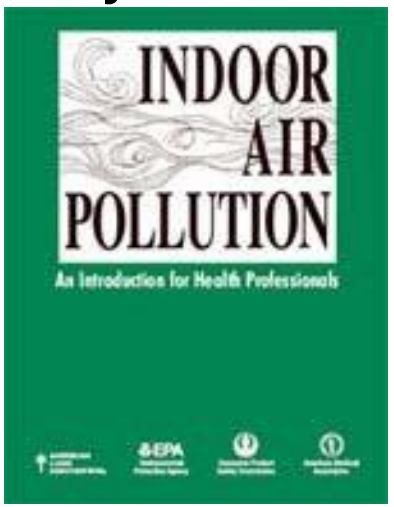
Indoor Air vs. Outdoor Air

- **Outdoor Criteria Pollutants**
  - **Ozone (from VOCs, NOx and light)**
  - **PM (2.5 and 10)**
  - **CO**
  - **NOx**
  - **SOx**
  - **Lead**
  - **HAPs**
- **VOCs regulated as ozone precursors**

- **Indoor Pollutants**
  - **Radon**
  - **CO**
  - **Tobacco smoke**
  - **Dust**
  - **Mold & mildew**
  - **Formaldehyde**
  - **Lead, asbestos**
  - **Pesticides**
  - **Ozone (from generators)**
  - **Organic gases (VOCs)**
- **VOCs suspected as toxics**

What's a VOC?

- **Outdoor**
  - **Any chemical that participates in atmospheric photochemistry and produces more ozone than ethane**
- **Indoor**
  - **Any volatile organic compound**
  - **"Formaldehyde, pesticides, solvents, cleaning agents"**
- **Why the difference?**
  - **"Studies* have shown…."**
    - **indoor VOC concentrations can be 2-5 times higher than outdoors**
  - **Formaldehyde emitted from wood products and some paints**
  - **EPA and others are blurring the line between VOCs and toxics**



***http://www.epa.gov/iaq/pubs/hpguide.html#VOCs**

Are VOCs Guilty By Association?

- **Are all VOCs toxic?**
- **Formaldehyde is a VOC and probable human carcinogen**
- **Risk = Hazard x Exposure**
- **Acute vs. chronic exposure**
  - **Acute = short-term (minutes – days)**
  - **Chronic = long-term (weeks-years)**
- **Acute vs. chronic hazards**
  - **Acute: irritation, nausea, CNS effects….**
  - **Chronic: cancer, reproductive effects…**
- **VOCs have been linked to asthma but the epidemiology link between VOCs and health effects is weak***
- **EPA-sponsored NAS study classified evidence linking VOCs to asthma as "inadequate"**

*** c.f. Fiedler et. al. Environ Health Perspect. 2005;113(11):1542-1548**

Regulatory Environment and Certifications

- **VOC regulations (e.g. SCAQMD) distinguish between:**
  - **Interior and exterior applications:**
    - **Flat, non-flat, floor paints: 50g VOC/liter**
    - **Concrete, traffic and IM coatings: 100g VOC/liter**
  - **Waterborne and solvent-borne coatings:**
    - **Clear wood finishes and lacquers: 275g VOC/liter**
  - **Some localities have passed laws mandating "green construction"**
- **Product Certifications and Organizations**
  - **For profit certification organizations and programs multiply**
    - **USGBC LEED, NAHB NGBS™, GreenSeal, GreenGuard…**
  - **GreenSeal is developing environmental standards for paints**
    - **http://www.greenseal.org/certification/environmental.cfm**
  - **Green Guides for Health Care v2.2**
    - **http://www.gghc.org/download/mgdocs.cfm?dir=GGHC%20Version%202.2**
- **Architects (AIA) and USGBC announce strategic alliances**
  - **May lead to new "green" paint mandates for construction**

Green Seal Standard for Paints & Coatings (GS-11)

- **Finalized May 12, 2008**
- **Received input from numerous stakeholders**
- **Standard establishes environmental requirements for some paints. Excluded from the standard are:**
  - **Stains, clears, recycled latex, aerosol and specialty coatings**
- **Also sets general and product-specific performance requirements**
- **Certain compounds and chemical classes are prohibited:**
  - **Carcinogens, mutagens, reproductive toxins, HAPs, ODCs, APEs, phthalates, formaldehyde donors, heavy metals, some tin compounds**
- **Volatile aromatic compounds limited to 0.5% of TVOC content**
- **VOC content limits are similar to SCAQMD Rule 1113**
- **Any compound with BP < 280°C is a VOC unless exempt**

CA DHS Specification for Testing Indoor Air

- **California Specification 01350**
  - **http://www.dhs.ca.gov/ps/deodc/ehlb/iaq/VOCS/LORS/Section01350_7_15_2004_FINAL_PLUS_ADDENDUM-2004-01.pdf**
  - **Test methods for paints, adhesives, and caulks**
  - **Environmental chamber test of VOC emissions**
  - **Test measures total VOCs, carcinogens and reproductive toxicants, and formaldehyde emissions**
  - **Paints applied to porous (wallboard) and non-porous (steel or glass) surfaces**
  - **Emissions measured 10 days after application at 24, 48 and 96 hours**
  - **Emissions factors then used to calculate "modeled" indoor air concentrations for a standard office or classroom**
  - **Concentrations compared to established OEHHA Reference Levels (RELs) for listed toxics (concentration considered safe)**

What's an REL?

- **"The acute reference exposure level (REL) is an exposure that is not likely to cause adverse effects in a human population, including sensitive subgroups, exposed to that concentration for 1h on an intermittent basis"**
- **"RELs are based on the most sensitive, relevant, adverse health effect reported in the medical and toxicological literature, and are designed to protect the most sensitive individuals in the population by the inclusion of margins of safety (OEHHA, 1999a)"**
- **Chronic RELs are usually based on animal studies (e.g. cancer)**
- **Acute RELs can be based on human data (e.g. irritation)**
- **RELs include several safety factors for sensitive subgroups, interspecies and LOAEL to NOAEL uncertainty factors**
- **These safety factors range from 6,000% to 60,000%**

OEHHA Reference Levels for Paint Components

Chemical Name (CAS #)	Chronic REL (µg/m3)	Acute REL (µg/m3)	Paint use
Diethanolamine (111-42-2)	3		additive in waterbased paints
Formaldehyde (50-00-0)	3	94	emitted from some paints
Ammonia (7664-41-7)	200		additive in latex paints
Triethylamine (121-44-8)	200	2,800	additive in waterbased paints
Toluene (108-88-3)	300	37,000	solvent
Ethylene glycol (107-21-1)	400		freeze thaw stabilizer in latex
Xylenes (m,o,p-isomers)	700	22,000	solvent
Ethylbenzene (100-41-4)	2,000		solvent
Isophorone (78-59-1)	2,000		solvent
Methanol (67-56-1)	4,000	28,000	solvent
n-Hexane (110-54-3)	7,000		solvent
Isopropanol (67-63-0)	7,000	3,200	solvent
Glycol ether PM (107-98-2)	7,000		solvent

EPA Capstone Report - EPA 600/R-01/093

- **National Risk Management Research Laboratory study**
- **Developed a standard method for indoor paint emissions testing**
- **Used ASTM D5116-97 small environmental chamber testing**
- **Models used to convert results to “typical” room concentrations**
- **Looked at VOC emissions from interior latex and alkyd paints**
  - **Solvents, MEKO, aldehydes**
- **Looked at substrate effects**
  - **Porous wallboard, glass, and white pine board**
- **Looked at short and long-term exposure levels**
  - **Acute vs. chronic risks**

Alkyd Paint Indoor Emissions

- **VOCs**
  - **Mostly aliphatic hydrocarbons in C8-C11 range**
  - **Some aromatic hydrocarbons in C9-C12 range**
  - **Main component monitored was decane**
- **MEKO (anti-skinning agent, 0.1-0.3 wt%)**
- **Aldehydes (oxidation products)**
  - **Formaldehyde**
  - **Higher aldehydes (hexanal, pentanal)**
- **Three semi-gloss alkyds were tested over an alkyd primer**

Alkyd Paint Emission Results

- **VOC emissions independent of substrates**
- **Decane chamber concentrations peaked 30 minutes after primer or paint application**
- **Increasing air exchange rate reduced decane concentrations**
- **90% of VOCs and MEKO were emitted in the first 10 hours**
- **100% of VOCs and MEKO were emitted in the first 24 hours**
- **Models estimated that MEKO concentrations peaked below the 10mg/m3 STEL and dropped below 0.01mg/m3 10 hours after painting**
- **Formaldehyde levels were close to the detection limit**
- **Hexanal levels fell below the odor detection threshold (4.5 ppb) after 130 hours**
- **Results show that alkyd paints are unlikely to pose an acute or chronic indoor health hazard**

GREENGUARD Emission Criteria for Children & Schools

Individual VOCs	≤1/100 TLV and ≤½ CA chronic REL
Formaldehyde	≤ 0.0135 ppm/13.5 ppb
Total VOCs	≤ 0.22 mg/m³
Total Aldehydes	≤ 0.043 ppm/43 ppb
Total Phthalates	≤ 0.01 mg/m³
Total Particles (≤10 µm)	≤ 0.02 mg/m³

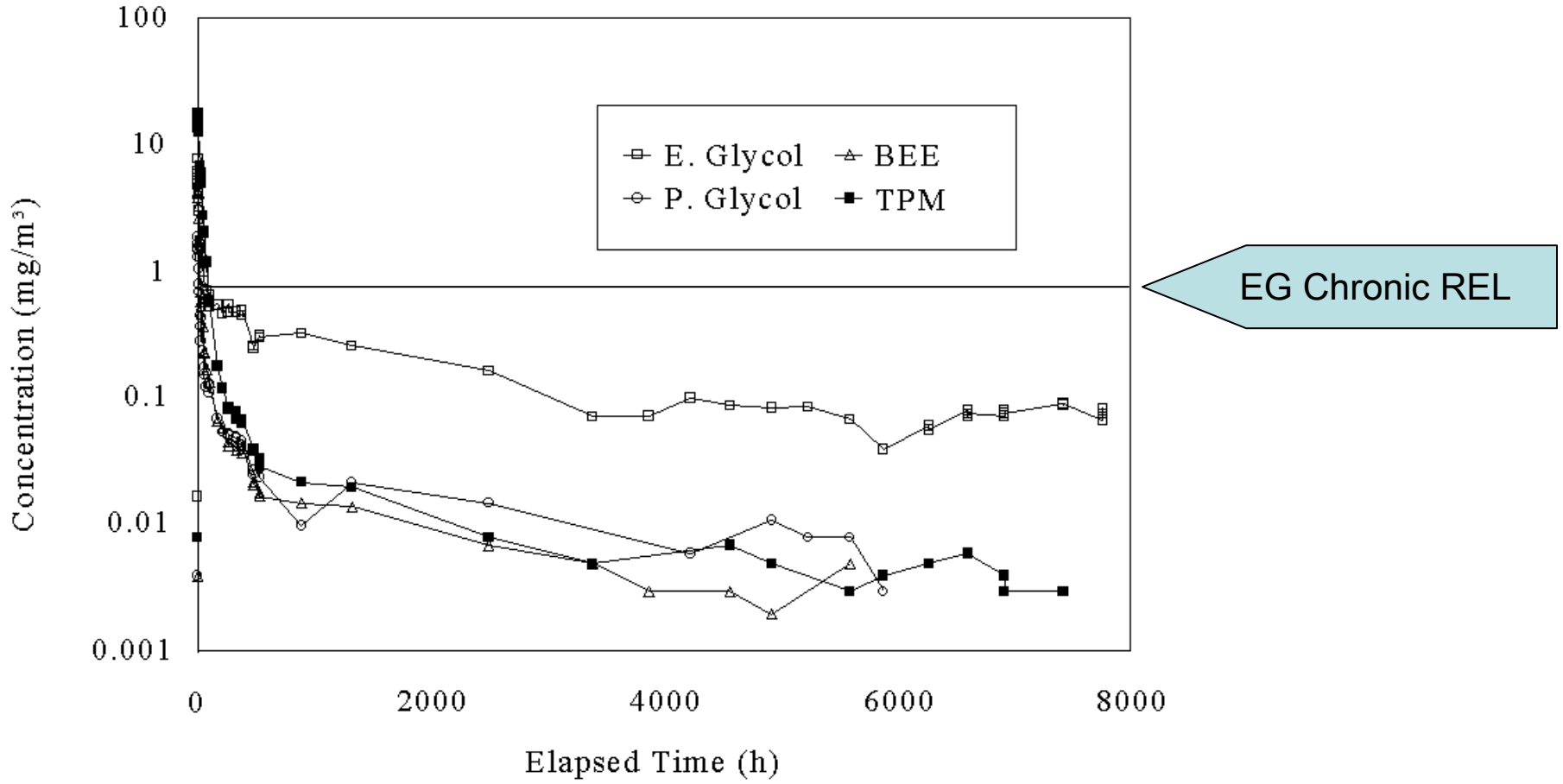
- **Most stringent GREENGUARD indoor air criteria**
- **Results to be met at 168 hours (7 days) after painting**
- **Alkyd paints in EPA Capstone report likely met top four criteria**
- **EPA speculation of potential "irritation and other health effects" from alkyd paints were not supported by results**

http://www.greenguard.org/Default.aspx?tabid=110

Latex Paint Indoor Emissions

- **One conventional (< 5%) and four low-VOC (<1%) latex paints tested on gypsum wallboard**
- **VOCs detected in both types of latex**
  - **Ethylene, diethylene, propylene and dipropylene glycols**
  - **Glycol ether DB**
  - **2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol®)**
- **Main VOCs were:**
  - **EG (2.4%) and Texanol® (1.4%) in conventional latex**
  - **DPG and glycol ether DB in low-VOC lateces**
- **Aldehydes were also emitted from two low-VOC latex paints**
  - **Formaldehyde, acetaldehyde and benzaldehyde**
  - **ASTM Standard D 5197 "Standard Test Method for Formaldehyde and other Carbonyl Compounds in Air (Active Sampler Methodology)"**

Long-Term VOC Emissions from Latex-Painted Wallboard



- **EG levels were below the chronic REL in the first 24 hours**
- **EPA concluded that it may take 3.5 years for all VOCs to be released**

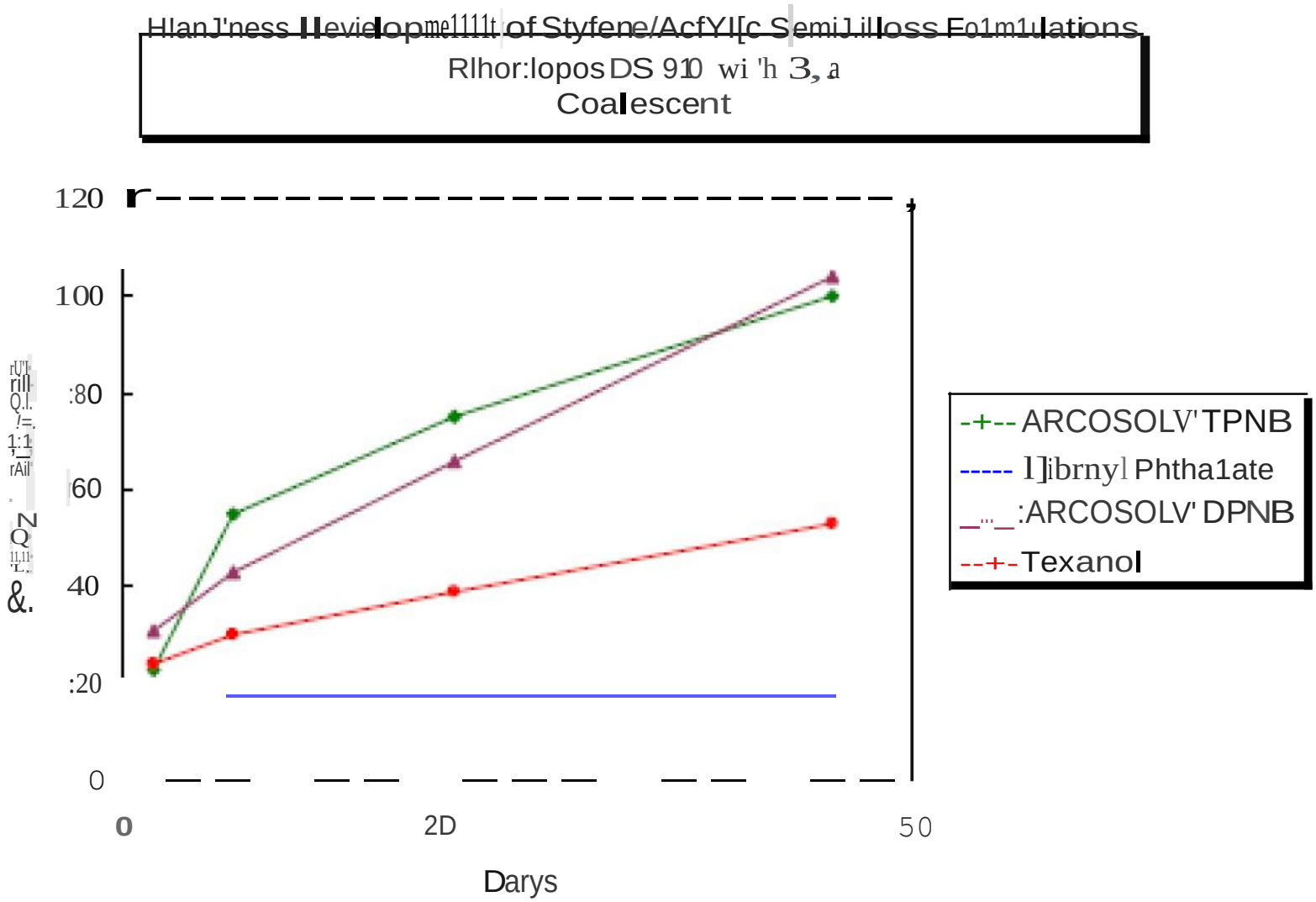
Latex Paint Emission Results

- **VOC emissions very dependent on substrates**
- **Wallboard showed “sink effect” for glycols**
  - **Only 20% emitted after 336 hours (14 days)**
  - **Low levels of EG emitted for years but below the chronic REL**
- **90% of VOCs were emitted from steel in the first two weeks**
- **Biocides, additives and binders were identified as the source of aldehydes**
- **Formaldehyde emissions can be eliminated by proper selection of raw materials**
- **Results show that typical latex paints are unlikely to pose an acute or chronic indoor health hazard**

Use of PG and Glycol Ethers in Latex Paints

- **PG is generally regarded as safe "GRAS" for human consumption**
- **Some PG-based glycol ethers are efficient coalescents for latex paints, are less persistent, less toxic, and less odorous than other coalescents**
- **Low and no-VOC paints often use softer resins so they can self-coalesce. This can affect:**
  1. **Dry times**
  2. **Dirt pickup**
  3. **Scrubability**
  4. **Durability**
- **Using PG instead of EG and PG-based glycol ethers instead of less volatile coalescents or plasticizer may improve:**
  1. **Indoor air quality**
  2. **Paint appearance**
  3. **Paint durability**

Coalescent Effect on Latex Film Hardness Development



http://www.lyondell.com/lyondell/techlit/techlit/2247.pdf

Indoor Air Testing of TBAC-Based Paints

- **Despite limited evidence that VOCs pose an indoor air quality risk, lower VOC content limits are being imposed**
- **Paint manufacturers may turn to exempt solvents to comply**
- **Two low-VOC TBAC-based indoor paints were tested**
  - **Clear conversion varnish for wood cabinets or flooring**
  - **White alkyd enamel for trim**
- **Testing performed at RTP labs: http://www.rtp-labs.com/**
  - **Sustainable products, "Green Building" and LEED chemical emissions testing using ASTM D5116 "Environmental Chambers"**
  - **California's Section 01350 "School Building Specifications" methods**
- **Additional tests to also look at short term TBAC emissions**

Clear Catalyzed Conversion Varnish

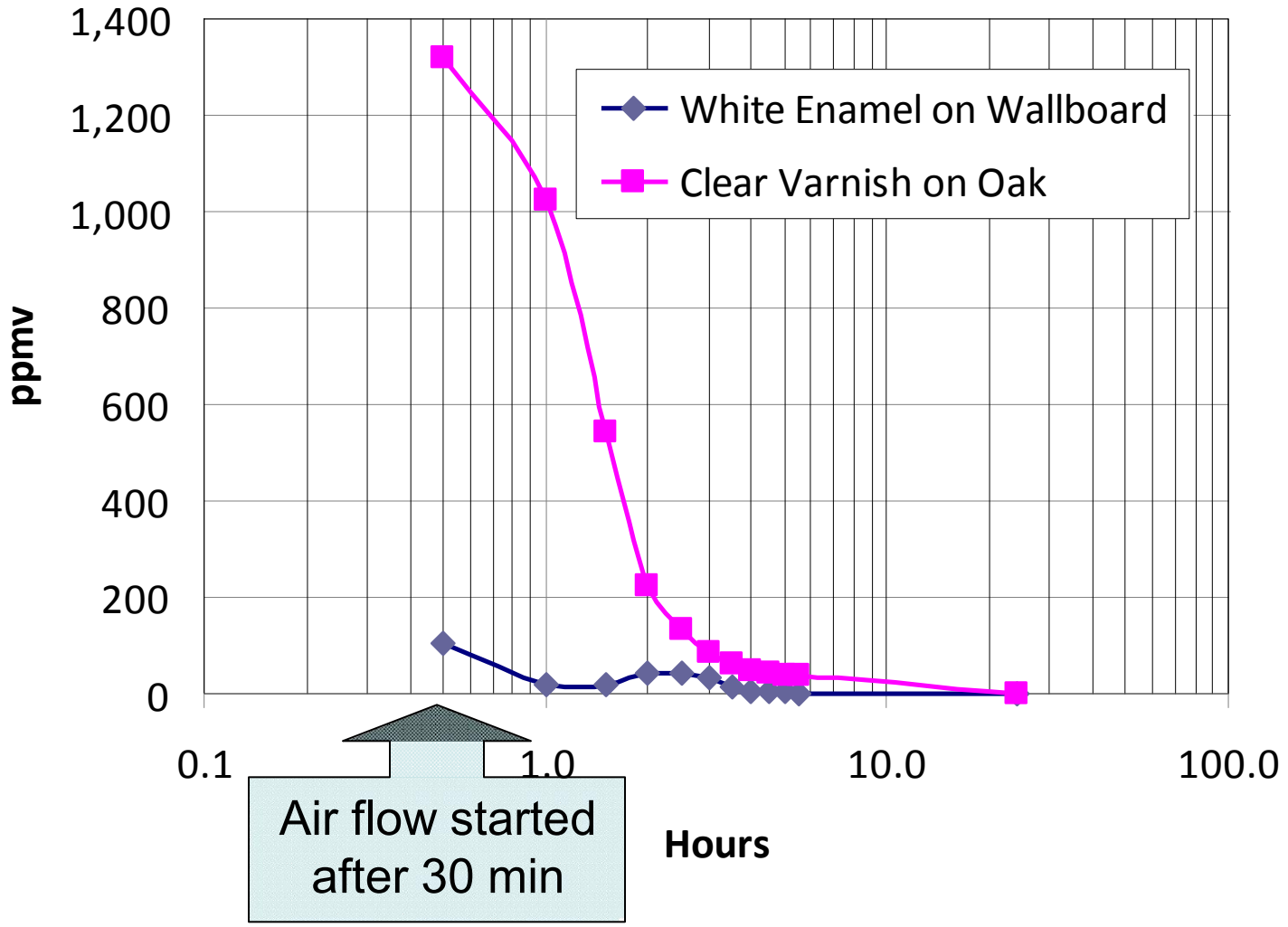
- **Used on kitchen cabinets, furniture and flooring**
- **Resin System:**
  - **Coconut alkyd: Beckosol® 12035-E2 (65% NV in 32/4 TBAC/A100)**
  - **Polyol: SAA-100 (100% NV)**
  - **Crosslinker: Cymel U80 (98% NV)**
- **Solvents used:**
  - **TBAC, n-butanol, MAK**
  - **Small amounts of Aromatic 100 and Isopropanol**
- **Varnish formulation**
  - **209 grams VOC/L**
  - **50wt% solids**
  - **Viscosity = 75 Cps**
- **Varnish applied to unprimed oak boards**

White Alkyd Enamel*

- **Used on wood trim, cabinets, walls**
- **Resin System:**
  - **Soy alkyd: Beckosol® 11081-E2 (70% NV in 26/4 TBAC/A100)**
- **White pigment: TiO_2**
- **Solvents used:**
  - **TBAC/mineral spirits 26/10, 2% methanol**
- **Enamel properties**
  - **250 grams VOC/L**
  - **62 wt% solids**
  - **Viscosity = 68 KU**
  - **PVC: 21%**
  - **Pigment to binder weight ratio: 0.93**
- **Enamel applied to unprimed gypsum wallboard**

***Thanks to Jeff Danneman of Reichhold for preparing the enamel paint**

TBAC 24-Hour Emission Profile from Alkyd Paints



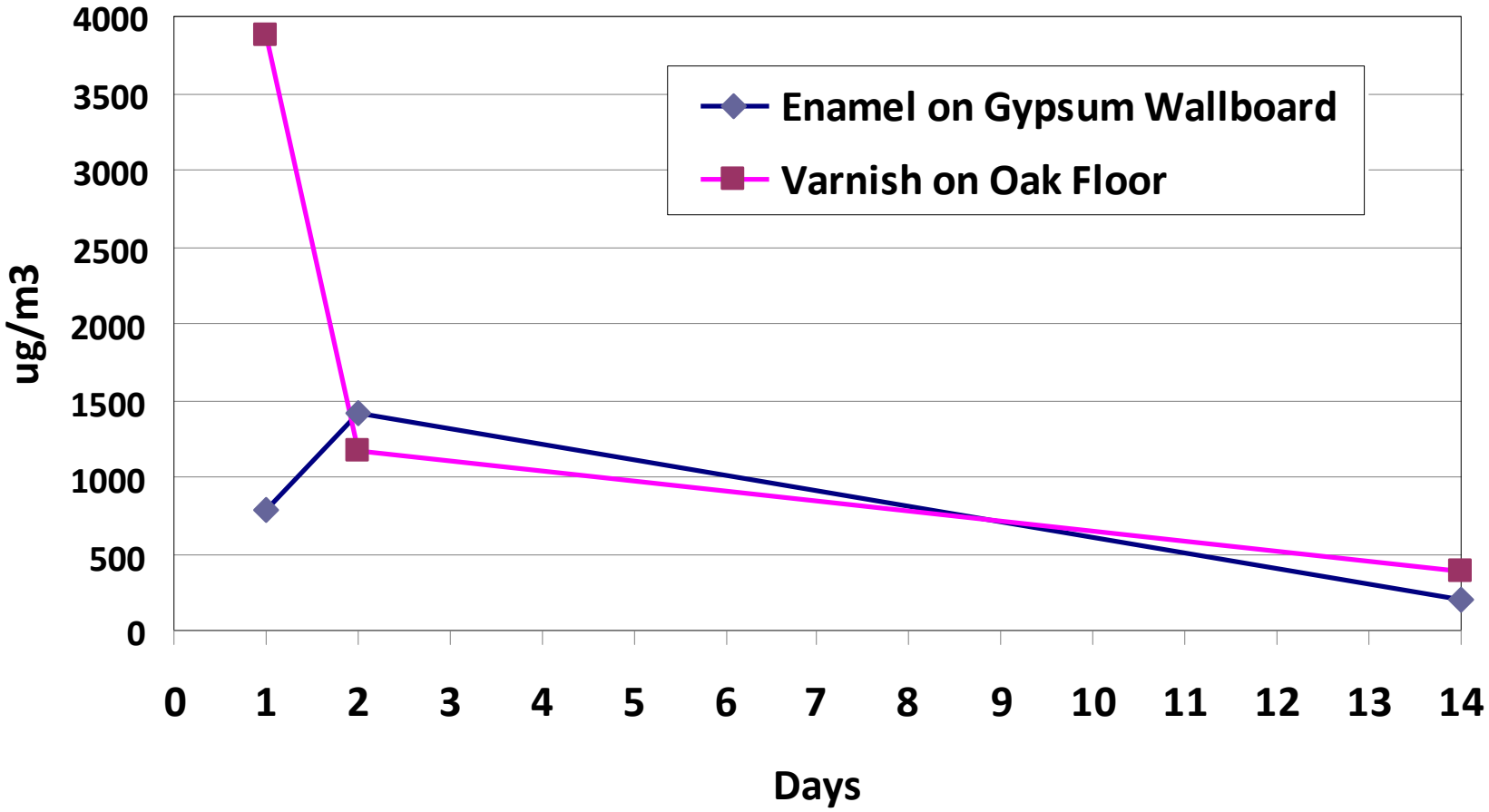
Samples placed in chamber immediately after roller application of two coats.

Samples left in closed chamber for 30 minutes prior to first measurement

TBAC Indoor Air Concentrations at 24 hours

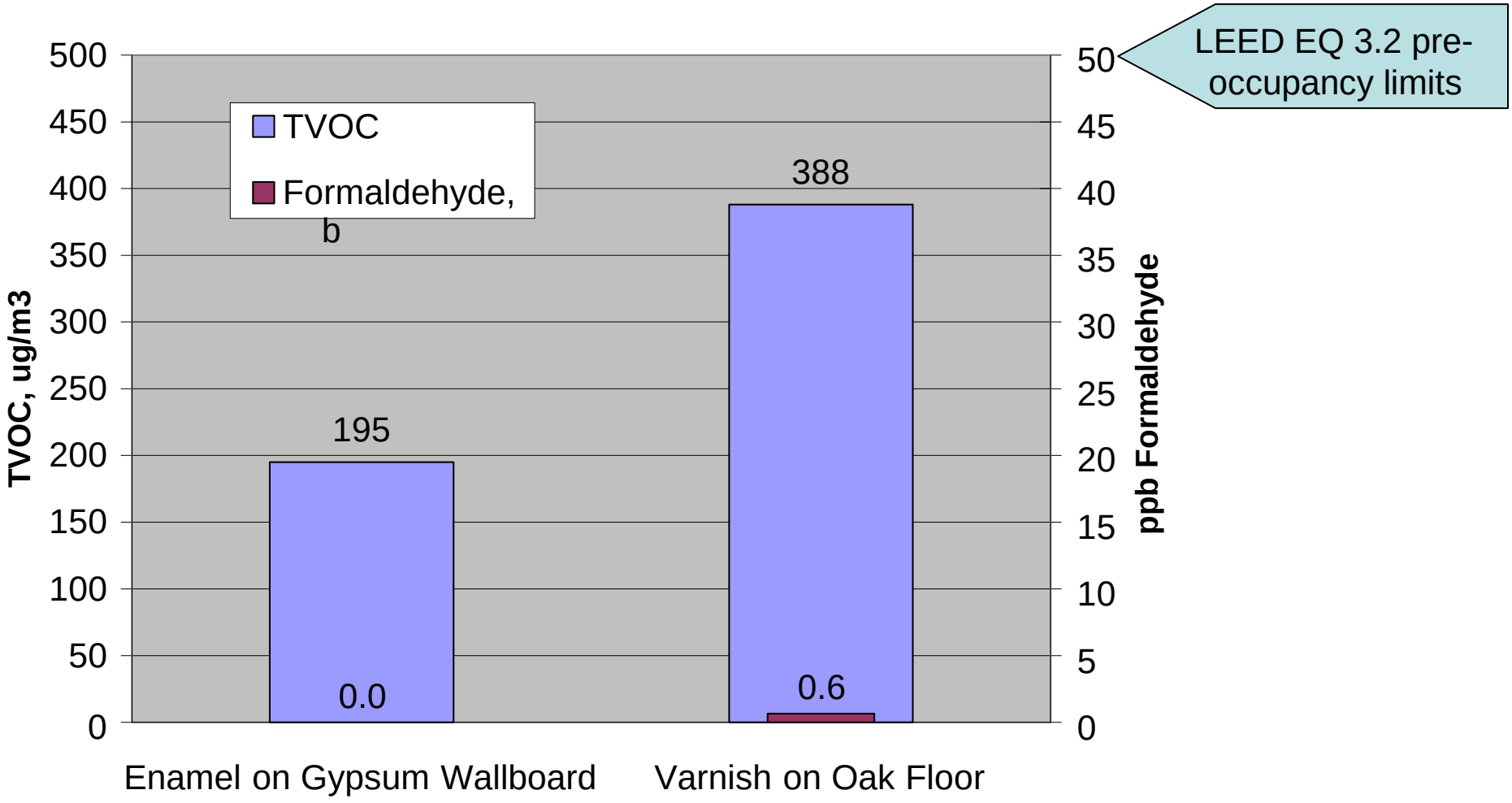
- **Model classroom parameters:**
  - **Room volume 231 m^3**
  - **Area painted: walls = 94.6 m^2; flooring = 89.2 m^2**
  - **Air exchange rate = 0.9 hr^{-1}**
- **Conversion varnish on floor (960 sf)**
  - **1.8 mg/m^3 (295 ppb) after 24 hours**
  - **Below ocular detection threshold (237 mg/m^3) and acute RfC (7 mg/m^3)**
  - **Close to chronic RfC of 1.4 mg/m^3 (mild CNS effects)**
  - **Above odor detection threshold of 8 ppb (38 $\mu g/m^3$)**
- **White enamel on walls (1,018 sf)**
  - **Below 50 $\mu g/m^3$ (11 ppb) after 24 hours**
  - **Approaching 50% odor detection level (38 $\mu g/m^3$)**

TVOC Levels in Model Classroom



- **Temporary sink effect with enamel on wallboard in first two weeks**
- **TVOC levels drop below level of concern prior to occupancy**

TVOCs and Formaldehyde in Classroom @14 Days



- Both paints qualify for LEED credits EQ 3.2 and EQ 4.2

Conclusions

- Indoor air quality concerns spawning “Green” certification standards and could lead to regulation
- Regulators attempting to link all VOCs to human health effects
- EPA’s own study does not support these concerns
- VOCs from alkyd paints dissipate quickly and do not to pose health risks to consumer or contractors
- TBAC dissipates very quickly from SB paints and could be a useful compliance and formulation tool
- VOCs emissions from latex paints applied to unprimed wallboard can continue for years but at levels below the chronic REL
- Some low-VOC latex paints produce formaldehyde and are less durable than conventional latex paint
- Best practice for Green Building IAQ may be to apply alkyd paint primer to wallboard followed by conventional latex paint with PG and volatile coalescents (e.g. PG-based glycol ethers)