

1 **Workshop on Interfacial Chemistry in Indoor Environments**
2 **July 17-18, 2007 University of California, Berkeley, CA**

3
4 **Report and Research Priorities**
5

6 The objectives of this workshop were to identify research needs and rank gaps in the
7 existing knowledgebase of indoor interfacial chemistry as it relates to human exposure to
8 air pollutants. Based on presentations and discussions, the participants identified the most
9 fruitful short-term research courses to follow, outlined medium and long-term research
10 goals, instigated new collaborations and identified key existing resources and necessary
11 improvements to the existing research infrastructure. The primary outcome is this Report
12 and Research Priorities statement for the National Science Foundation and the California
13 Air Resources Board. Other outcomes may include an editorial or regular journal article.
14 With students making up nearly one quarter of the participants, an equally important
15 outcome was to inspire the next generation of researchers and build a foundation for
16 continued improvements in the quality of the built environment.

17 **INTRODUCTION**

18 **Interfacial and surface chemistry in indoor environments**

19 Interfacial chemistry greatly influences human exposure to reactants and products in
20 indoor environments. As an example of one of the more dramatic instances, ozone
21 reactions on indoor surfaces result in a 2 to 10 fold reduction in occupant exposure to
22 ozone (Sabersky et al. 1973; Weschler et al. 1989; Lee et al. 1999). Chemistry that occurs
23 at interfaces is remarkably important despite the tiny amount of volume taken up by the
24 thin layer of molecules coating indoor surfaces. This is because 1) the available surface-
25 area is large relative to the total volume of a typical building, 2) surfaces tend to enhance
26 reaction rates relative to that in the gas-phase because species sorb and concentrate on
27 surfaces, increasing the apparent overall reaction rate and 3) unique compositions and
28 morphologies at surfaces can promote some reactions or promote selectivity in reaction
29 pathways. Adsorption extends the average residence time for species in a building,
30 resulting in a higher probability of reaction than the same species in a gas.

31 Weschler (Weschler, 2006) persuasively argues that indoor ozone chemistry may
32 be partially responsible for the effects of ambient smog ozone: significant adverse health
33 effects are associated with even small incremental increases in ambient ozone.

34 Fortuitously, most advances in this research area have revolved around ozone-surface
35 chemistry. Ozone chemistry has been studied on nearly every relevant surface in indoor
36 environments. Ozone uptake rates on surfaces, regardless of the chemistry, have been
37 quantified on carpets, paint, tiles, concrete, wood, and glass (Grontoft 2002; Grontoft
38 2004; Grontoft et al., 2004a; Grontoft et al., 2004b; Morrison and Nazaroff, 2000;
39 Morrison and Nazaroff, 2002; Reiss et al., 1995). The primary loss mechanism for ozone
40 in indoor volumes is surface reactions, causing the indoor levels to be about 1/3 of
41 outdoor levels. Ozone oxidation of interfacial organic matter generates volatile aldehydes
42 and acids from carpet (Morrison and Nazaroff, 2002), soiled surfaces in homes (Wang
43 and Morrison, 2006) and in a simulated aircraft cabin (Wisthaller et al., 2005; Weschler

44 et al., 2007), paint (Reiss, 1995) and ventilation duct materials (Morrison et al., 1998).
45 Coined “secondary emissions”, the resulting concentrations of these volatile products are
46 large enough to have health and comfort consequences. Ozone also reacts with chemicals
47 intentionally or unintentionally applied to surfaces. Known ozone-reactive chemicals
48 include nicotine from cigarette smoking (Destailats et al., 2006b), pesticides such as
49 cypermethrin (Segal-Rosenheimer and Dubowski, 2007), and terpenes that are found in
50 cleaning or other scented products (Flemmer et al., 2007). Recently, researchers have
51 shown that cleaning products enhance ozone uptake at surface, long after the event has
52 taken place (Singer et al., 2006a). A variety of other classes of reactions have also been
53 studied. Plasticizers such as diethylhexylphthalate (DEHP) can be hydrolyzed (Lundgren
54 et al., 1999) and hydrolysis products may be associated with asthma (Norback et al.
55 2000). Acid-base chemistry at surfaces has been shown to release stored nicotine (Webb
56 et al., 2002) and modify surface characteristics so that sorption of volatile species is
57 altered (Ongwande et al., 2005). Early work on NO_x - surface chemistry showed that
58 NO₂ will react with water on smog chamber surfaces to generate HNO₃ and volatile
59 HONO (Sakamaki et al., 1983; Pitts et al, 1984; Jenkin et al., 1988). Pitts et al. (1985a)
60 showed that this chemistry also occurs on indoor surfaces and can generate HONO levels
61 that exceed outdoor levels when gas burners are used (Pitts et al., 1989). Recently
62 Ramazan et al. (2006) showed that nitric acid may further participate in chemistry, and
63 photolysis, that releases NO and HONO. Thus indoor surfaces can act as a sink for NO₂,
64 a reservoir for HNO₃, and a source HONO and possibly NO. Nitrate radicals (Weschler et
65 al., 1992) may also be an important oxidant in the low-light environment of indoors
66 spaces.

67 There are large gaps in our understanding of interfacial indoor chemistry.
68 Although many studies have been made of ozone chemistry, little is known about the
69 influence of environmental conditions on this chemistry. Only a fraction of the predicted
70 volatile products have been identified and few studies have attempted to identify the
71 resulting low-volatility products of this chemistry that remain on surfaces. NO_x
72 chemistry is still poorly understood, yet the possibility of generating carcinogenic nitro-
73 aromatics (Pitts et al., 1985b; Arey et al., 1986; Pitts et al., 1987) deserves more attention.
74 These research voids are only a few of the gaps evaluated in this workshop. Filling these
75 gaps will allow us to improve indoor environmental quality by reformulating consumer
76 products, targeted control of reactants and products, or designing new architectural
77 materials and coatings.

78 Many recommendations for future research were put forward in workshop
79 discussions; the following summarize research priorities with notable consensus:

- 80
- 81 ■ A molecular level understanding of physical and chemical processes occurring at
 - 82 indoor surfaces
 - 83 ■ Composition and morphology of indoor surfaces and interfaces
 - 84 ■ Health consequences of indoor air/interfacial chemistry
 - 85 ■ Reactions occurring at the human interface and with human residues (e.g. skin
 - 86 oils) and bioeffluents

87 **RESEARCH PRESENTATIONS**

88 The workshop presentations and the questions raised thereby are summarized here and
89 organized, loosely, by the following subject area: **ozone-organic chemistry, hydrolysis,**
90 **inorganic chemistry, controls, other perspectives.**

91 **Ozone chemistry**

92 Context and motivation

93
94 An active research area has been the interaction of ozone with various indoor surfaces
95 and specific chemicals at interfaces. Charles Weschler put this research in context in his
96 plenary presentation, “Indoor chemistry's impact on public health: suggestive studies”.
97 He suggests that epidemiological correlations between ozone and morbidity or mortality
98 are due, in large part, to indoor exposures to ozone and the byproducts of its reaction with
99 other species indoors (Weschler, 2006). He estimates, conservatively, that indoor
100 exposure to ozone (that originates outdoors and is transported indoors) is 2/3 to 3 times
101 greater than outdoor exposure to ozone, while indoor exposure to ozone oxidation
102 products is commonly in the range of 1/3 to 6 times greater than outdoor exposure to
103 ozone. While it is thought that indoor levels of reaction products may correlate with
104 outdoor levels of ozone, this hypothesis has not been evaluated in field settings. Products
105 of this chemistry include carcinogens (formaldehyde, acrolein), irritants (aldehydes,
106 ketones, acids), free radicals, and oxidation products of concern (e.g. pesticide oxidation
107 products). Indoor exposure to chemicals and their reaction products was evaluated by
108 William Nazaroff in his plenary presentation, “Exposure Consequences of Indoor Surface
109 Chemistry”. He showed that the “intake fraction” of ozone reaction products is high
110 (~4000 per million) compared with typical intake fractions for typical outdoor sources
111 (~10 per million). Based on recent research findings that ozone reacts rapidly with human
112 skin oils on indoor surfaces, Nazaroff suggested that ozone exposure may be significantly
113 reduced due to reactions with the human body and clothing; it follows that exposure to
114 volatile reaction products would be increased. Combined, Weschler and Nazaroff argue
115 that there is an urgent need to understand transformation rates, product generation rates
116 and mechanisms and other dynamics associated with ozone chemistry in indoor
117 environments.

118

119 Fundamentals.

120

121 Barbara Finlayson-Pitts presented an overview of interfacial phenomena associated with
122 ozone reactions with organic mono-layers (Dubowski et al., 2004). She questions the
123 “reaction probability” as a useful metric for characterizing ozone rates on surfaces
124 because the value *depends* on ozone concentration. The dependency is consistent with
125 Langmuir-Hinshelwood kinetics, but there is a need for a better molecular-level
126 understanding to discern the true mechanisms. One unusual outcome of these studies is
127 the finding that the second-order interfacial reaction rate for ozone with organics is
128 roughly equal, regardless of the organic species (Pöschl et al., 2001; Mmereki et al.,
129 2003). Why? And will this result extend to “real” surfaces?

130

131

132 Aerosol composition.

133

134 Secondary organic aerosols, generated oxidatively, may be similar in composition,
135 functionalization and, hygroscopicity to coatings on indoor surfaces. Sergey Nizkorodov
136 presented his recent research to unravel the composition of secondary aerosols generated
137 as a result of ozone reacting with limonene. Combining electrospray ionization mass
138 spectrometry (ESI-MS) with Kendrick analyses (Reinhardt et al., 2007), Dr. Nizkorodov
139 derived the detailed molecular formulae of the aerosol components. The composition is
140 consistent with primary and secondary oxidation pathways. However, Nizkorodov
141 suggests that it will be sufficient in the future to determine functional group composition
142 of aerosols and by extension, surface coatings, rather than detailed molecular structure
143 information.

144

145 Reactions with noteworthy surface species.

146

147 Hugo Destailats reported that ozone reacts with nicotine to produce a variety of
148 oxidation products including N-methyl formamide, formaldehyde and cotinine
149 (Destailats et al., 2006). This “aging” of nicotine on surfaces reduces nicotine re-
150 emission rates, but co-adsorbed water protects nicotine from oxidation. Yael Dubowski
151 reported on ozone reactions with cypermethrin (Segal-Rosenheimer and Dubowski,
152 2007), a synthetic pyrethroid insecticide used commonly to control pests in homes. Dr.
153 Dubowski showed that the reaction leaves irritating and toxic compounds such as 3-
154 phenoxybenzaldehyde on surfaces. Further, volatile products include phosgene, an
155 extremely toxic compound. Under dry atmospheric conditions, kinetic studies suggest a
156 21 day half-life for cypermethrin. It is unclear if toxic levels of byproducts are generated
157 under typical indoor conditions.

158

159 Ray Wells and Jason Ham reported on the use of a Field and Laboratory Emission Cell to
160 study ozone chemistry with squalene (a component of skin oils) on glass and alpha-
161 terpineol (a fragrance component in many products) on PVC tile and glass (Flemmer et
162 al., 2007). They detect di-carbonyl species generated from both reactions, including
163 glyoxal, methylglyoxal and 4-oxopentanal. These di-carbonyl compounds are thought to
164 be particularly irritating. They observed products unique to heterogeneous ozone-
165 terpineol chemistry demonstrating that products and yields may be influenced by the
166 substrate.

167

168 Field and laboratory studies of mixed media.

169

170 Hong Wang studied ozone reactions on indoor surfaces present in 5 homes in Rolla, MO
171 over a 1.5 year period (Wang and Morrison, 2006; Wang and Morrison, 2007). They
172 found that ozone uptake and secondary yields are consistent with laboratory results for
173 carpet and other studied materials. The most reactive surface is kitchen countertop,
174 probably due to cooking oils. Over the 1.5 year period, no significant change in uptake
175 rates were observed, but yields were significantly lower in winter. Ozone uptake rates for
176 carpet in older homes was lower than in newer homes, but for kitchen counter tops, there
177 was no observed trend related to the age of the home.

178

179 Brett Singer reported on LBL studies of primary emissions of, and ozone reactions
180 occurring with, cleaning products used in a typical manner in a large laboratory chamber
181 (Singer et al., 2006a; Singer et al, 2006b). They observed that sorbed terpene
182 hydrocarbons and terpene alcohols can react with ozone to form secondary pollutants.
183 Use of a plug-in air freshener resulted in a large reservoir of sorbed, ozone-reactive
184 terpenes. Sorbed compounds accounted for half of ozone reactions in air freshener
185 experiments, even though the air freshener had been deployed for only a few days;
186 continuous use could result in greater relative reactivity. Pine oil residues were also
187 ozone reactive.

188
189 Charles Weschler reported on O₃ reactivity experiments in an occupied, simulated aircraft
190 cabin (Wisthaller et al., 2005; Wisthaller et al., 2007; Weschler et al., 2007). When O₃
191 was present, the concentrations of aldehydes, ketones & organic acids were much larger.
192 They concluded that people are major O₃ sinks – larger than carpet, seats and dirty HEPA
193 filter combined. The human component of secondary emissions include acetone, nonanal,
194 decanal, 6-MHO, geranyl acetone and 4-OPA They also found that the presence of O₃
195 and its oxidation products adversely affected 12 of 29 self-reported symptoms based on
196 questionnaires from occupants.

197
198 In small-chamber laboratory research, Beverly Coleman studied ozone reactions with all
199 major aircraft cabin surfaces, including clothing, upholstery, carpet, and plastic cabin
200 materials (Coleman et al., 2007). All surfaces contribute to O₃ consumption and
201 byproduct formation, and ozone aging and regeneration were observed. Reaction
202 byproducts and yields were consistent with those reported by Weschler in a simulated
203 aircraft cabin, including C1-C10 saturated aldehydes and squalene oxidation products.
204 Yields were observed to be higher at higher RH, an important result given the very low
205 humidity conditions in aircraft cabins, in contrast to higher humidity conditions at
206 clothing and human surfaces.

207
208 Glenn Morrison reported on ozone reactivity studies of human hair in a small fixed-bed
209 reactor (Pandrangi and Morrison, 2007). His group found that the ozone reaction
210 probability on human hair is approximately 10⁻⁴. Model analysis suggests that ozone
211 uptake in the head region is mass-transport limited; rapid ozone uptake could result in
212 lower-than-anticipated exposures to ozone. Oxidation products observed were consistent
213 with reactions with sebum (squalene and fatty acids). Conditioners appear to increase
214 ozone uptake and unwashed hair yields more reaction products.

215

216 **Hydrolysis**

217 In his plenary presentation, Dr. Weschler discussed the role of hydrolysis on the
218 transformation of plasticizers, pesticides, flame retardants and coalescing agents
219 (Lundgren et al., 1999; Norback et al. 2000). Hydrolysis can generate toxins (e.g. mono-
220 ethylhexylphthalate from hydrolysis of DEHP), odors (isobutyric acid) and chemicals
221 associated with asthma (phthalic anhydride). Since hydrolysis reactions are mediated by
222 local pH and moisture conditions, a better understanding of these and other relevant
223 properties in materials is needed.

224 Richard Corsi reported on an intensive study of paint components, with a focus on mass
225 closure of texanol isomers (2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate or TMPD-
226 MIB) (Lin and Corsi, 2007). They varied paint types and substrates and recovered
227 texanol from air emissions and from substrates. In the process of these experiments, they
228 identified hydrolysis products of TMPD-MIB, including isobutyric acid, emitted in the
229 first few days after application. But not all paints act the same way, and he also
230 emphasized the impact of external factors such as acidity, temperature and the water
231 content of substrates.

232

233 **Inorganic chemistry**

234

235 Melissa Lunden reported on an intensive study of the characteristics and dynamics of
236 indoor aerosols of outdoor origin during winter (Lunden et al., 2003). A key outcome was
237 that ammonium nitrate aerosols evaporate at time scales comparable with air exchange.
238 Evaporation reduces the size and mass of aerosols and generates gaseous ammonia and
239 nitric acid. Irreversible uptake of nitric acid on surfaces reduces gas phase levels and
240 drives the evaporation of ammonium nitrate. This study highlights the importance of
241 indoor interfacial interactions on the concentration and composition of indoor aerosols,
242 even those that originate from outdoors.

243

244 In a classic study of inorganic reactions at indoor interfaces, Pitts et al. (1989), showed
245 that HONO was generated as a result of NO₂ interactions with indoor surfaces. Mike
246 Kamboures and Jonathan Raff of AirUCI explained that this was a result of hydrolysis of
247 N₂O₄ on surfaces. They also report on experimental studies and *ab initio* calculations of
248 the possibility that HONO is also formed as the result of thermal or photolysis of nitric
249 acid on surfaces. They conclude that photolysis is possible, but that thermal pathways to
250 the production of HONO from nitric acid are unlikely.

251

252 **Controls**

253

254 Indoor air pollution controls should consider interfacial chemistry, but might also *use*
255 interfacial chemistry to clean air. Results of several research projects were presented in
256 this context.

257

258 Richard Corsi reported on a several-year study of “extreme chemistry” taking place on
259 building materials that have been subjected to very high levels of ozone or chlorine
260 dioxide for disinfection (Poppendieck et al., 2007a). Both species are effective
261 disinfectants, but also react readily with some indoor surfaces. They showed that high
262 rates of reactant removal on some materials (ceiling tiles, office partitions, wallboard)
263 may significantly reduce the efficacy of disinfection by reducing local disinfection
264 concentrations. Ozone tends to generate more measurable oxidation products than
265 chlorine dioxide and byproduct emissions tend to persist for months. Chlorine dioxide
266 generates detectable levels of chlorinated compounds, but mechanisms are unclear.

267

268 Several groups have been studying ozone interactions with filters and with the particulate
269 matter that is collected on filters. Lara Gundel, Jeffrey Siegel, Charles Weschler and
270 Richard Corsi outlined results that are suggestive of filters influencing air quality: BASE

271 study results indicate that aldehydes may be generated on filters. Previous studies
272 indicate that ozone exposure reduces the “acceptability” of air from the filter (Bekö et al,
273 2006). Ozone is consumed by dirty filters, but filter materials age with continued
274 exposure. Filters coated with kitchen oils are particularly effective at removing ozone
275 (Zhao et al., 2007). Time-scale analysis suggests that diffusion within attached particles
276 limits overall conversion rates. Dr. Siegel explained that there is little awareness in
277 industry that ozone reactions on filters may be important. Specifically, 1) their customers
278 don't complain about odors or other detectable aspects of the problem, 2)there are no
279 regulations or standards that require ozone removal from ventilation (other than the 62.1
280 standard for high ozone areas which is not enforced), 3)their customers don't demand
281 ozone removal, and 4)they don't believe that it is an important issue (i.e. there is a gap
282 between the research and the dissemination).However, some at ASHRAE have been
283 working to broaden ASHRAE standard 62.1 to make intentional ozone removal (e.g.,
284 activated carbon filters) more widespread in commercial buildings.

285

286 Hugo Destailats discussed LBL research on UV photocatalytic devices used to
287 decompose VOCs in indoor environments (Hodgson et al., 2007). Using a realistic
288 mixture of VOCs (including alkanes, alcohols, aromatics, terpenes, carbonyl and
289 halogenated compounds), they showed that removal efficiency ranged from <10% for
290 PCE to >75% for alcohols. Formation of potentially harmful byproducts (aldehydes) in
291 the device can be attributed to oxidation of certain alcohols, ketones and terpenes.

292

293 Franz Geiger reported on Northwestern University efforts to better understand the
294 physical chemistry of interfaces. Using Chemical Ionization Mass Spectrometry (CIMS),
295 Geiger's group was able to precisely measure the enthalpy of binding of acetone on TiO₂,
296 a substrate commonly used for photocatalytic decomposition of indoor air pollutants.
297 They showed that acetone is physisorbed and that adsorption time scales can range from
298 10's to 100's of minutes (Schmidt et al., 2006; Schmidt et al., 2007). In work related to
299 the ozone chemistry reported by Drs. Pitts and Dubowski, Geiger showed that terpenes
300 attached to specially functionalized surfaces react faster with ozone than in the gas phase,
301 but only initially.

302

303 **Other perspectives**

304 Hal Levin, of the Building Ecology Research Group, discussed architectural perspectives
305 on indoor chemistry, material selection and testing. He explained that architects “don't
306 want to understand it” and they want experts to “just tell us what to do”. They want
307 simple answers to complex questions. Further, architects often are not responsible for
308 choices of furnishings and other materials, e.g. contractors and builders typically choose
309 materials for residential buildings. They usually receive advice *from* retailers, and
310 manufacturers tell buyers what they want to hear. Material product development is driven
311 by marketing, not science or health concerns. Environmental certification (e.g.
312 Greenguard) does consider primary emissions, by diverse criteria, but does not consider
313 the consequences of chemical transformations. Although many certification schemes are
314 based on chamber testing of materials, there are concerns that existing emissions testing
315 is not adequate to predict installed performance with respect to the effects of interfacial
316 chemistry which could be both substantial and important in many commonly occurring

317 conditions. The oversimplified pass-fail criteria of the certification programs now in
318 place do not screen out all hazardous products because they do not currently employ any
319 criteria for many hazardous chemicals known to be emitted from common building
320 products. Also, there is no screening of cleaning and re-finishing products and processes
321 under current emissions testing and certification programs. These products can result in
322 exposures far greater than those from the materials to which they are routinely applied
323 during the service life of the building material (Levin, 1999).

324 Peggy Jenkins, of the California Air Resources Board, outlined the organization's
325 priorities and probable future funding in the indoor air quality research areas. She
326 explained that climate change is the priority at ARB for now, but one or two projects on
327 indoor air quality are typical per year. Among the indoor research priorities (tentative)
328 are: indoor chemistry / surface interactions, nanoparticles in products, and ozone
329 emissions from in-duct air cleaners. Research must make the link to ARB programs and
330 needs including relevance, significance for exposure and risk assessment, or mitigation
331 and control measures. She highlighted two recent successes in regulating indoor air
332 pollution: a formaldehyde emission standard for manufactured wood products, and a
333 regulation targeting ozone generating air cleaners.

334 **GROUP DISCUSSIONS AND RECOMMENDATIONS**

335 **Long-term research priorities**

336 After a series of presentations on Day 1, the participants were asked as a single group to
337 generate an un-ranked list of research needs (See Appendix C for this list in its original
338 form). Then the participants were segregated into four groups, each composed of roughly
339 equal numbers of chemists, engineers, other specialties and students. In a break-out
340 session, each group was tasked with generating a short list of key issues to be resolved or
341 “grand challenges”, resources available and funding possibilities. The following synthesis
342 is based on the break-out discussions.

- 343 1. Molecular level understanding of physical and chemical processes. A theme
344 common to most groups was that a molecular level understanding of
345 physiochemical processes on real surfaces will ultimately be necessary to
346 understand macroscopic phenomena such as exposure.
 - 347 a. Molecular level insights need to be gained into
 - 348 i. Important transformative processes such as ozone and free radical
349 oxidation, hydrolysis, dissociation, ozonide decomposition, etc.
 - 350 ii. Sorption, desorption and hysteresis
 - 351 iii. Surface and interfacial species aging
 - 352 iv. Aqueous film chemistry and the role of water at interfaces
 - 353 v. Time scales of processes
 - 354 vi. The role of interfacial processes as they affect nucleation,
355 condensation and the properties of aerosols including SOA and
356 SIA.
 - 357 b. There should be focus on the use of models designed to interpret
358 controlled experiments so as to quantify parameter values and to test
359 current understanding. Modeling as a tool for making predictions about
360 indoor environments is less valuable owing to the idiosyncratic
361 characteristics of buildings and the relative lack of importance in pinning
362 down what is going on in any one specific building. Models designed to
363 predict probability distribution functions of concentrations in classes of
364 buildings could be useful but may not yet be feasible.
 - 365 c. Certain fundamental parameters are unknown for many common surface
366 types. These include: Surface area, pH on surfaces under typical
367 conditions, water uptake isotherms, aging of various surfaces, etc.
 - 368 d. More effort is needed to close material balances to determine the ultimate
369 fate of chemicals in buildings. Further, *all* relevant surfaces need to be

370 studied, including the human surface, surfaces surrounding all entry
371 pathways and the ventilation system.

372 e. To reach these goals, the community will have to develop and/or apply
373 new analytical techniques to study/characterize the chemistry and physics
374 of surfaces. Certain methods hold promise in providing useful
375 information, e.g., PTR-MS, desorption electrospray ionization (DESI),
376 ATR (attenuated total reflectance) spectroscopy, or hyperspectral sensors.

377 2. Composition and morphology. A common theme was the need to have a much
378 better understanding of the composition and morphology of indoor materials and
379 their interfaces.

380 a. The composition of substrates (and their engineered coatings), such as
381 PVC flooring, painted drywall, carpet, and upholstery, can vary widely
382 even within substrate types; yet compositional information is rarely
383 investigated in detail or reported.

384 b. The composition of the material overlaying substrates, such as dirt, dust,
385 oils, reaction residues, and salts, is also poorly understood. There have
386 been some efforts made (e.g. Butt et al., 2004) to analyze these coatings,
387 but participants expressed concern that traditional methods will not
388 capture the true composition. For example, moderately stable ozonides or
389 epoxides may be transiently present on real surfaces, but transformed to
390 other species during extraction and analysis.

391 c. Morphology, including surface area and pore size distribution, will also
392 influence interfacial phenomena. Yet traditional methods of measuring
393 morphology are difficult to apply to indoor materials. For example, many
394 indoor materials outgas volatiles making BET measurements difficult or
395 impossible. Further, vacuum analysis of indoor materials necessarily
396 changes the surface composition, and perhaps the morphology.

397 3. Health and indoor air chemistry. The number of pollutants and potential pollutants
398 observed or predicted to be found in indoor environments vastly out number the
399 chemical species that have been evaluated for toxicity or other health outcomes.
400 There needs to be some mechanism to rank species for scrutiny based on existing
401 toxicological data or potential toxicity as estimated from structure-activity
402 relationships. Further, interactions between chemists, engineers and toxicologists
403 are necessary to identify species for future toxicological assays.

404 4. Physical and chemical property database. Progress would be expedited if there
405 was a convenient, exhaustive, and trustworthy body of data that would be
406 available to scientists, regulators, and newcomers to the field. It would not only
407 provide a convenient reference, but also help identify areas that require research.
408 Serving this purpose would be a database that includes all that is known to date
409 regarding physical-chemical properties of surfaces and heterogeneous reactions.
410 This could be assembled by a committee of experts (physicists, engineers,

411 chemists, etc.) in a manner similar to the NASA/JPL evaluations of Chemical
412 Kinetics and Photochemical Data for Use in Atmospheric Studies or the
413 information provided by IUPAC's subcommittee for Gas Kinetic Data Evaluation.
414 The database would be assembled with a high level of scientific rigor and could
415 include information on: 1) the chemical and physical properties and morphology
416 of commonly found building materials and indoor surface types; 2) properties,
417 such as vapor pressures, for commonly occurring indoor chemicals; 2) data on the
418 composition, surface areas, porosity, pore distribution; 3) kinetic data on water
419 uptake and desorption / adsorption kinetics of various materials; 4) kinetics data
420 on common surface reactions. Unlike NASA/JPL evaluations, the database could
421 include data that is more phenomenological, rather than fundamental in nature.
422 For example, data on specific reactions on specific surfaces are useful for
423 understanding macroscopic behavior, but may not be fundamental or unvarying
424 even for a class of indoor surfaces.

425 5. Standard test methods and metrics. Existing test methods do not generally account
426 for emissions due to chemical transformations. To help generate consistent and
427 useful data on the interfacial chemistry of building materials and their coatings, it
428 was recommended that standard test methods be developed for products and
429 materials as a basis for ratings/public information. Test methods should be
430 developed for ozone oxidation and other kinds of interfacial chemistry. Further, a
431 set of uniform metrics needs to be identified, such as fundamental reaction rate
432 constants on surfaces.

433 **Short to medium term research priorities**

434 After a series of presentations on Day 2, the participants were asked as a single group to
435 generate a list of Short Term research needs and “low-hanging fruit”. The following
436 synthesis is based on this group discussion.

437 The participants did not rank these; the order does not signify priority.

438 1. Ozone chemistry

- 439 a. The effect of humans. An emerging body of evidence points to reactions
440 of ozone with human surfaces and with skin oils transferred to indoor
441 surfaces (Weschler et al., 2007; Coleman et al., 2007; Pandrangi and
442 Morrison, 2007). These reactions are fast and ozone uptake may be mass
443 transfer limited in the region around the body. To assess the impact of
444 these reactions on “true” exposure to ozone and its oxidation products, the
445 following has been recommended: Simultaneous measurement of ozone
446 and oxidation products in the well-mixed air of an occupied class room,
447 outside the classroom and in the breathing zone of occupants. Also
448 recommended was a broader survey of breathing zone measurements in
449 the population.
- 450 b. Controls. The participants recommended that activated carbon filtration
451 (and other interventions) be assessed for its ability to simultaneously
452 reduce ozone and oxidation product exposure to occupants. It was also

453 suggested to combine this research with an assessment of productivity
454 and/or absenteeism.

455 c. Pesticides. Pesticide oxidation has been shown to generate toxins (e.g.
456 phosgene in Segal-Rosenheimer and Dubowski, 2007). A priority will be
457 to determine (experimentally and theoretically) the conversion rates and
458 products associated with ozone reactions with pesticides most commonly
459 used in and around buildings.

460 d. Architectural materials. Architectural materials can reduce ozone
461 concentrations indoors, but also are a source of oxidation products. A
462 review of the present knowledge of ozone uptake rates and oxidation
463 product generation rates is needed to make recommendations regarding
464 inner surfaces in buildings (Morrison et al., 2006). This preliminary
465 assessment would then allow for more directed research towards the use of
466 existing or “to be developed” architectural materials with the goal of
467 improving indoor air quality.

468 2. Human bioeffluents. Human bioeffluents directly influence indoor air quality
469 (odors), but also contribute to reactivity (unsaturated organics), acidity (CO₂),
470 basicity (ammonia) and may influence other chemical properties of surfaces.
471 Therefore, the participants recommend determining the composition and
472 distribution of emission rates of bioeffluents from humans, pets and other living
473 organisms in buildings.

474 3. Building materials and coatings. The participants recognized a need for a more
475 complete inventory of the composition, physical and chemical properties of
476 building materials, furnishings and coatings used during regular maintenance.
477 Related to material composition, concern was expressed over the use of fly-ash in
478 concrete that may increase pH and promote hydrolysis reactions.

479 4. Key list of measures, variables and outcomes: In a related area, the participants
480 suggested that we, as a community, generate a list of key measures, outcomes and
481 variables. As an example, the “deposition velocity” is a useful comparative tool
482 for certain systems, but is not as readily transferable across systems as the concept
483 of “reaction probability”.

484 5. State of Knowledge Reviews. Some participants felt that it is now time for several
485 State of Knowledge Reviews to help inform and interpret research in this area:

486 a. Sorption in indoor environments
487 b. Nature of indoor surfaces including composition, chemistry and
488 morphology.
489 c. Nature of water on indoor surfaces and in indoor environments

490 6. HVAC and interfacial chemistry. The participants recognized that there are a
491 variety of direct and indirect mechanisms by which heating, ventilation and air
492 conditioning systems take part in, or influence, interfacial chemistry in indoor
493 environments. Three specific questions were posed

494 a. How can HVAC systems be optimized to control interfacial chemistry?
495 b. How does recirculation influence surface chemistry occurring within
496 HVAC systems?
497 c. What is the nature of surface chemistry in naturally ventilated vs
498 mechanically ventilated buildings? A white paper on this subject was
499 recommended.

- 500 7. Photocatalysis. There is growing interest in the use of photocatalytic coatings on
501 surfaces. If a sufficiently large area of indoor environments is coated with an
502 effective photocatalytic material, then VOC concentrations could be reduced
503 several fold. However, some participants felt it is prudent to provide early
504 guidance, based on our existing understanding of interfacial chemistry, transport
505 mechanisms, and exposure models. Two questions were raised:
506 a. Will surface coatings ever be sufficiently effective to compete with
507 existing methods of source reduction?
508 b. Will formaldehyde, acetaldehyde and other products of incomplete
509 oxidation increase in concentration to unacceptable levels?
- 510 8. Vehicles: Americans spend more time in their vehicles than outdoors and the
511 vehicle surface area to volume ratio is very large. Thus, pollution exposure
512 mediated by interfacial processes in vehicles could be important. However, little
513 is known at this time about interfacial phenomena in vehicles.
- 514 9. Extreme chemistry. Ozone and chlorine dioxide are being used to deodorize and
515 disinfect buildings, and its use is rising. Given the reaction products and damage
516 caused, the extent of these problems need to be assessed:
517 a. By-product formation: Field data on gas-phase oxidation products would
518 be useful in assessing the probable air quality effects. Many of these
519 products are likely to be difficult to identify and quantify with traditional
520 techniques, so newer analytical methods may be needed.
521 b. Corrosion: Oxidation can result in the degeneration of building materials,
522 furnishings, circuitry and artwork. Material damage, especially damage to
523 plumbing or electrical power systems, can result in major building
524 damage, injury or death. Therefore, before-and-after analysis of
525 microscopic and macroscopic effects should be studied.
- 526 10. Other recommendations:
527 a. The Leadership in Energy and Environmental Design (LEED) or Green
528 Building Rating System is becoming widespread since its inception in
529 1998. There has been concern that indoor air quality is poorly understood
530 and is undervalued in the program. It was recommended that the scientists
531 and engineers of the indoor air community become more active in LEED.
532 b. Participants also recommended that there be better communication
533 between engineers and scientists. Workshops like this one can help
534 engender this communication. But an actively networked community, with
535 more frequent contact would help drive progress in this field.

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APPENDIX A

800

801

802

803 **Workshop presentations**

804 July 17, 2007 Morning 542 Davis Hall

805

806 8:00 Welcome and introductions

807 *Glenn Morrison, Univ. of Missouri-Rolla*

808 8:10 Plenary: Indoor chemistry's impact on public health: suggestive
809 studies

810 *Charles Weschler, UMDNJ-DTU*

811 Moderator: *Richard Corsi*

812 8:50 Interfacial chemistry: environmental examples

813 *Barbara Finlayson-Pitts, Univ. of California, Irvine*

814 9:30 Composition of indoor secondary aerosol particles

815 *Sergey Nizkorodov, Univ. of California, Irvine*

816 10:00 Break-time Carlson room and patio, 7th Floor Davis Hall

817 10:20 Aging and re-emission of nicotine sorbed to model surfaces

818 *Hugo Destailats, LBL and Arizona State University*

819 10:40 Pesticides aging in the atmosphere: heterogeneous oxidation of
820 cypermethrin

821 *Yael Dubowski, Technion-Israel Institute of Technology*

822 11:00 System for reactant delivery to surfaces

823 *J. Raymond Wells, NIOSH*

824 11:20 Surface chemistry reactions of α -terpineol with ozone and air on
825 a glass and a vinyl tile

826 *Jason Ham, NIOSH*

827 11:40 Realistic use experiments to study cleaning product-ozone
828 chemistry

829 *Brett Singer, Lawrence Berkeley National Laboratory*

830 12:00 Lunch Berkeley restaurants

831

832 July 17, 2007 Afternoon 542 Davis Hall

833

834 Afternoon session moderator: *J. Ray Wells*

835 1:00 Impact of surfaces on ozone-terpene conversion rates (originally scheduled but
836 cut from program in the interests of time)

837 *Glenn Morrison, Univ. of Missouri-Rolla*

838 1:20 Ozone-surface reactions in five homes: uptake rates,
839 product yields and trends

840 *Hong Wang, Univ. of Missouri-Rolla*

841 1:40 Ozone consumption and volatile byproduct formation from surface
842 reactions with aircraft cabin materials and clothing fabric
843 *Beverly Coleman, Univ. of California, Berkeley*

844 2:00 Surface chemistry in a simulated aircraft cabin: the importance of
845 occupants
846 *Charles Weschler, UMDNJ-DTU*

847 2:20 Ozone uptake rates and byproduct yields for human hair
848 *Glenn Morrison, Univ. of Missouri-Rolla*

849 2:40 Break Carlson room and patio, 7th Floor Davis Hall

850 3:00 Group discussion (listing of important future research topics)

851 4:00 Break-out discussions (small group ranking of topics)

852 5:00 Break-out reports

853 ~ 5:30 End

854 July 18, 2007 Morning Heyns Room, Faculty Club

855

856 8:00 General announcements
857 *Glenn Morrison, Univ. of Missouri-Rolla*

858 8:10 Plenary: Exposure consequences of indoor surface chemistry
859 *William Nazaroff, Univ. of California, Berkeley*

860 Morning session moderator: *Hugo Destailats*

861 8:50 Hydrolysis of phthalates and paints
862 *Richard Corsi, Univ. of Texas, Austin*
863 *Charles Weschler, UMDNJ-DTU*

864 9:10 Ammonium nitrate aerosol dynamics in indoor environments
865 *Melissa Lunden, Lawrence Berkeley National Laboratory*

866 9:30 The role of nitric acid complexes on surfaces in indoor and
867 outdoor chemistry
868 *Jonathan Raff and Mike Kamboures, Univ. of California, Irvine*

869 10:00 Break Faculty Club

870 10:20 Extreme surface chemistry
871 *Richard Corsi, Univ. of Texas, Austin*

872 10:40 Interaction of ozone with PM on filters in HVAC systems
873 *Lara Gundel, Lawrence Berkeley National Laboratory*

874 11:00 Panel discussion: chemical transformations on filters
875 *Richard Corsi, Univ. of Texas, Austin*
876 *Lara Gundel, Lawrence Berkeley National Laboratory*
877 *Charles Weschler, UMDNJ-DTU*

878 11:20 What is the filtration community doing about indoor air
879 chemistry (and what should they be doing)?
880 *Jeff Siegel, Univ. of Texas, Austin*

881
882 11:40 Performance of ultraviolet photocatalytic oxidation for indoor air
883 cleaning applications
884 *Hugo Destailats, LBL and Arizona State University*

885 11:50 Designing surfaces to control indoor pollutants
886 *Franz Geiger, Northwestern University*

887 12:20 Working Lunch Faculty Club
888
889 July 18, 2007 Afternoon
890 Afternoon session moderator: *Beverley Coleman*

891 1:40 Architectural perspective on indoor chemistry, material selection
892 and testing
893 *Hal Levin, Building Ecology Research Group*

894 2:00 California Air Resources Board: research directions
895 *Peggy Jenkins, California Air Resources Board*

896 2:20 Break Faculty Club

897 2:40 Group discussion and ranking of priorities

898 4:30 Conclude workshop
899 *Glenn Morrison, Univ. of Missouri-Rolla*

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APPENDIX B

902 **Alphabetical list of participants, broad technical area and affiliation**

903	R.J. Briggs	University of Texas-Austin
904		PhD Student, Economics
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906	Beverly Coleman	University of California-Berkeley
907		PhD Student, Environmental Engineering
908		
909	Richard Corsi	University of Texas-Austin
910		Professor, Environmental Engineering
911		
912	Hugo Destailats	LBL and Arizona State University
913		Staff Scientist, Chemistry
914		
915	Yael Dubowski	Technion – Israel Institute of Technology
916		Assistant Professor, Civil and Environmental Eng.
917		
918	Andrea Dunker	Virginia Tech
919		PhD Student, Environmental Engineering
920		
921	Barbara Finlayson-Pitts	University of California-Irvine
922		Professor, Chemistry
923		
924	Franz Geiger	Northwestern University
925		Associate Professor, Chemistry
926		
927	Lara Gundel	Lawrence Berkeley National Laboratory
928		Scientist, Chemistry
929		
930	Zhishi Guo	Environmental Protection Agency
931		Scientist, Chemistry
932		
933	Jason Ham	National Institute for Occupational Safety and Health. Scientist, Chemistry
934		
935		
936	Alfred Hodgson	LBL and Berkeley Analytical Associates
937		Scientist, Chemistry
938		
939	Diana Hun	University of Texas-Austin
940		PhD Student, Environmental Engineering
941		
942	Peggy Jenkins	California Air Resources Board
943		Manager, Indoor Exposure Assessment
944		
945	Mike Kamboures	University of California-Irvine
946		Post-doc, Chemistry
947		
948	Daria Kibanova	National Autonomous University of Mexico
949		PhD Student, Chemistry
950		
951	Hal Levin	Building Ecology Research Group
952		Research Architect
953		
954		

955	Melissa Lunden	Lawrence Berkeley National Laboratory
956		Scientist, Environmental Engineering
957		
958	Linsey Marr	Virginia Tech
959		Assistant Professor, Environmental Engineering
960		
961	Fatemeh Mizbani	Berkeley High School
962		High school science teacher
963		
964	Glenn Morrison	University of Missouri-Rolla
965	(organizer)	Associate Professor, Environmental Engineering
966		
967	William Nazaroff	University of California- Berkeley
968		Professor, Environmental Engineering
969		
970	Sergey Nizkorodov	University of California-Irvine
971		Assistant Professor, Chemistry
972		
973	Thomas Phillips	California Air Resources Board
974		
975		
976	Dustin Poppendieck	Humboldt State
977		Assistant Professor, Environmental Engineering
978		
979	Jonathan Raff	University of California-Irvine
980		Post-doc, Chemistry
981		
982	Shi Shu	University of Missouri-Rolla
983		PhD Student, Environmental Engineering
984		
985	Jeffrey Siegel	University of Texas-Austin
986		Assistant Professor, Environmental Engineering
987		
988	Brett Singer	Lawrence Berkeley National Laboratory
989		Scientist, Environmental Engineering
990		
991	Emma Smith	Yale
992		PhD Student, Chemistry
993		
994	Jed Waldman	California Department of Public Health
995		
996		
997	Hong Wang	University of Missouri-Rolla
998		PhD student, Environmental Engineering
999		
1000	Michael Waring	University of Texas-Austin
1001		PhD student, Environmental Engineering
1002		
1003	Ray Wells	National Institute for Occupational Safety and
1004		Health
1005		Scientist, Chemistry
1006		
1007	Charlie Weschler	UMDNJ and DTU
1008		Professor, Chemistry and Environmental Engineering
1009		
1010	Lily Wu	California Air Resources Board
1011		Agency representative, Physiology

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1013 *Statistics*

1014 Total: 36 active participants

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1016 Affiliations: 9 universities, 3 federal agencies or national laboratories, 2 California state
1017 agencies, 1 high school, 1 business

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1019 Composition: 9 students, 2 post-docs, 8 federal or state scientists, 11 university
1020 professors, 4 California state agency representatives, 1 research architect, 1 high school
1021 teacher, 14 women, 22 men.

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APPENDIX C

Unranked list of research needs based on group discussions

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1. Oxides of nitrogen with organics (thermo & photochemical processes)
2. Aqueous phase reactions: Do they behave like bulk water or different?
3. We need to better understand the nature of the water film
4. Governing molecular level principles that explain what we see. Understand the processes and what controls them. Get to the point where we can then generalize the chemistry.
5. The degree to which these processes occur in bulk or on surfaces
6. Remediation and heterogeneous catalysis
7. Relative contribution of exposure due to body chemistry
8. Lifetime of intermediates on and in materials
9. Temperature difference between surface and bulk
10. The nature of sorption processes
11. S/V missing data on this for houses, building materials, etc.
12. Dermatological effects of reactive species to the skin
13. Dynamics of reservoirs
14. We need to build a practical model to quantitate or estimate exposures indoors. Parcel / indoor GCM models. Merge CFD with chemistry models. Need better model than a continuously stirred reactor box model. Will need to generalize. It needs to be multicompartmental. Needs to be parameters for heterogeneous chemistry.
15. Use field studies to verify estimates that are produced by theoretical models. Field studies are needed to develop a data set to help verify exposure estimates.
16. Functional group analysis
17. Inexpensive analytical techniques need to be developed that can analyze chemical composition or physical properties under atmospherically or indoor relevant conditions.

- 1070 18. We need to keep an eye on trends in the composition of materials. e.g., green
1071 materials and nanomaterials, or what is the state of the art in additives to materials.
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- 1073 19. Develop standard test methods for interfacial chemistry.
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- 1075 20. What should we be characterizing? Prioritize
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- 1077 21. SOA generation indoors. More work needs to be done to characterize this.
1078
- 1079 22. Need a reactivity index or rating system for various compounds / materials
1080
- 1081 23. Look at other oxidants: H_2O_2 and ClO_2
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- 1083 24. Study the integral mechanisms
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- 1085 25. What are the relevant timescales for some of these mechanisms and which are most
1086 important? Look at the big picture.
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- 1088 26. Close the material mass balance on the yields. If we are analyzing only the gas phase
1089 we are missing a lot. It should be standard by now to also analyze the surface
1090 species.
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- 1092 27. Develop materials or use materials that take up / scrub ozone and chemicals instead of
1093 emitting ozone.
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