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Letter to the Editor regarding "Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work"

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INTRODUCTION

The recently published article, *Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work,*[1] is scientifically flawed and misleading. In preface, the authors do not disclose at least two important conflicts of interest: 1) While acknowledging that CRC Industries ("CRC") prepared the "historical" Brakleen brake cleaner blends and paid for the field simulation, the authors did *not* mention that CRC Industries has been a frequent defendant in benzene exposure lawsuits concerning its Brakleen brake cleaners ("Brakleen"), and 2) Instead of disclosing *specifically* that one of the authors, Dr. Williams, has served as a testifying expert for CRC in benzene exposure lawsuits,[2] the authors acknowledge *only in general terms* that she is a testifying expert in benzene exposure cases. Obviously, these facts matter and should have been disclosed. The reported benzene content of the so-called "historical" Brakleen (1.6 parts per million), said to have contained 38% toluene, is improbably low and almost certainly in error given the benzene contents and other relevant properties of the three commercial grades of toluene that may be purchased in bulk. Importantly, the finding that "no detections of benzene were found" in any sample taken during eight exposure simulations is misleading (and unsurprising) in light of the unrealistically low benzene content of the "historical" Brakleen that was sprayed in the simulations. In responding to my letter, the authors should address sworn testimony given by Dr.

Williams that nitration grade benzene (which has no ASTM specification for minimum purity or maximum benzene content) is used to manufacture brake cleaner products. Neither ALS Global (C. Amidon, personal communication, May 3, 2018) nor CRC Industries (A. Selisker, personal communication, May 3, 2018) responded to information requests germane to the preparation and analysis of "historical Brakleen."

Misleading "Spiked" Brakleen Blends

Brakleen blends B and C in the present study, which CRC ostensibly prepared by "spiking" the "historical" Brakleen A with benzene, had "targeted" benzene contents of only 100 parts per million (ppm) and 1,000 ppm, respectively. The article thus creates the false impression that non-chlorinated Brakleen products in the stream of commerce always contained no more than 1,000 ppm benzene (corresponding to an important threshold concentration in benzene exposure litigation). Because commercial brake cleaning products general utilize nitration or industrial grade toluene (discussed below), their benzene contents can be more than100-fold and 10-fold higher than reported in the article for blends B and C, respectively.

Toluene and Benzene Content of "Historic" Brakleen

The "historical" Brakleen blend A that CRC formulated reportedly contained 38% toluene (unclear if this is by volume or weight). As noted, recipes for aerosol brake cleaners generally utilize "nitration grade" toluene, which contains as much as 2.29% benzene (molar basis).[3-5] "Industrial grade" toluene is less pure and contains as much as 4.48% benzene (molar basis).[3,6] In practice, toluene products sold as nitration grade are sometimes the less-pure industrial grade. For instance, a recent material safety data sheet (MSDS) for nitration grade toluene communicates an initial boiling point of 109°C

(corresponding to industrial grade toluene) and a benzene content of up to 2.5% (25,000 ppm).[7] The per unit volume cost of toluene varies according to its purity grade. The purest (99.9%) grade of toluene that is commercially available in bulk is TDI Feedstock,[8] which is specified to contain up to 300 ppm benzene. Analytical grade toluene (costing $125 per 150 ml septum bottle) contains up to 100 ppm benzene. Since a 20-ounce size Brakleen aerosol is sold for less than five dollars, CRC would of course find it cost prohibitive to use analytical grade toluene in its Brakleen products.

Given the recipe for "historical" Brakleen A, CRC would have had to use toluene that contained *less than 1 ppm benzene* to account for the benzene content of Brakleen A, as reported in the article. Simply put, there is no such toluene on the market - not even high priced analytical grade toluene sold in pint size amber bottles. If the authors disagree, they can say so and provide proof in their response. Curiously, CRC did not respond to an email in which I inquired about the grade and properties of toluene it used to prepare "historical" Brakleen blend A. (A. Selisker, personal communication, May 3, 2018) The authors, who appear to have blindly accepted the analytical result communicated to them, offer no documentation (e.g., certificate of analysis, initial boiling point, paraffin content) for the toluene grade CRC used in formulating the "historical" Brakleen blend A. Nor do they even comment on the issue. In fact, the authors do not say whether CRC (or an outside lab it engaged) ever conducted analytical testing to measure the benzene content of Brakleen in commerce or of the toluene used by CRC to manufacture it. Certainly, such measurements would have been useful to include in the article for comparison purposes. I note that if industrial grade toluene versus nitration grade toluene versus TDI feedstock toluene versus analytical grade

toluene were present at 38% by volume in blend A, one would expect to see as much as the following respective benzene concentrations in "historical" Brakleen A (ppm by volume): 15,200 ppm, 7,600 ppm, 114 ppm, and 38 ppm. Thus, if the 38% of "historical" Brakleen A consisting of toluene was the analytical grade, one would anticipate up to 24-fold more benzene in blend A than is reported in the article.

While the authors identified peer-reviewed NIOSH 1501 as the test used to quantify airborne exposures, the only reference in the article to the unidentified ALS Global testing method used to determine the benzene contents of bulk Brakleen was that it involved "gas chromatography coupled with a flame ionization detector." That is analogous to providing a chocolate cake recipe that says only that one should bake the cake in an oven. Based on the foregoing, I conclude it was unwise for the authors to have blindly reported the bulk benzene content results communicated to them.

Air Speed Measurements

In Figure 5, the authors graphically present air speed measurements made with a factory-calibrated thermal anemometer (TSI VelociCalc 9535) for Scenario 1 (closed bays doors) and Scenario 2 (open bay doors). The figure shows that most air speed readings were less than 30 ft/min with frequent "zero" readings and, as expected, the readings were higher overall with the bay doors open. The authors seem not to believe their own measurements and classify as "erratic" readings below 30 ft/min. They cite a 10-year-old American Conference of Governmental Industrial Hygienists (ACGIH) ventilation manual (reference 34) to support the idea that their anemometer was unreliable at measuring low air speeds. However, what the manufacturer TSI says about the reliability of measurements made with its calibrated anemometer is far more relevant

than a general statement in an ACGIH manual. Moreover, based on the air speeds reported in the cited Wilson, et al. study (reference 26), the authors likely knew from the start that low air speeds were expected. In turn, if they questioned the reliability of the TSI instrument, they had ample opportunity to acquire a more accurate anemometer. Reference 26 does not characterize the low measured air speeds (well below 30 ft/min) as being indicative of "stagnant" conditions. It was misleading for the authors to have done so without justification (aside from admitting they logged "many of the recordings as zero" because of poor performance of their anemometer).

Mischaracterizing Exposures as "Typical" and "Worst Case"

The title of the article, and the assertion that the simulations corresponded to "typical use of an aerosol brake cleaner" are offered absent independent verification and seems based on the authors' opinion. To determine "typical use," one would need to look at the variation in aerosol brake cleaner use by a sizable random sample of brake mechanics performing the same type of brake job(s); the present study involved exactly one brake mechanic in one location. The authors themselves allude to a "paucity" of this kind of data. Exposure determinants that pertain to "typical use" are (i) the total volume of solvent sprayed per wheel in a specified time period, (ii) the fraction of sprayed solvent that runs off into a drip basin or onto the floor, (iii) the temperature of the sprayed surface (which need not be the same as the air temperature), and (iv) the proportion of the task period (say, 15 minutes) that the mechanic's face is close to the evaporating solvent and the timing of cleaning. The authors' report data related to item (i) in their Figure 3, but report no data for items (ii)-(iv). By the timing of cleaning, I refer to whether the mechanic begins cleaning a surface immediately after spraying it, or whether the

mechanic walks away after spraying the surface to perform a different task or to let the solvent act on grime, and then returns to the sprayed surface some minutes later. The former timing would lead to a higher breathing zone solvent exposure intensity compared to the latter timing.

The authors' assertion that the simulations were performed under "worst-case conditions compared to typical work environments" misrepresents the circumstance that "typical work environments" vary shop by shop, by work location within a given shop, and by indoor air temperature, which can vary with time of year. The further a work bay is located from an open garage door, the lower the air speeds in the bay; in a large multi-bay shop, a given work bay easily can be greater than 40 feet from the nearest garage door. During the present study, outdoor air temperatures ranged from 70—90°F, and indoor air temperatures ranged from 82—96°F. In Phoenix, AZ, the average outdoor high temperature in July is 106°F without air cooling, the corresponding average indoor high air temperature would be at least 106°F.

Given the "paucity" of relevant exposure data the authors discuss, there is no basis for their misleading conclusion that exposures in some of the simulations correspond to "worst case" exposures in other workplaces (which may number in the hundreds if not thousands) for which there is no information about exposure factors and patterns of product use. In fact, there is no basis for concluding the simulations represented "worst case" exposures even in the location where the simulations were conducted.

Misrepresentation about American Industrial Hygiene Association (AIHA) Accreditation

The authors fail to reveal that ALS Global was not accredited by the AIHA to perform bulk sample analyses for benzene. Unfortunately, their wording left the distinct and inaccurate impression that ALS Global's AIHA accreditation - which only applied to air sample analyses - extended to bulk sample analyses. ALS Global did not respond to my email (C. Amidon, personal communication, May 3, 2018) in which I inquired about the detection limit and precision of the test, whether it was peer reviewed, and whether ALS Global is accredited by AIHA to perform the test. The ALS Global website indicates only that the company is AIHA-accredited to analyze air samples.

CONCLUSION

In my opinion, this article illustrates information bias ("misclassification of exposure estimates") that is prevalent in many industry-funded studies.[9] Many of these studies (including the present one) report findings favorable to defendant companies funding the studies, even if the findings do not comport with real world scientific facts. Important false impressions offered in the current paper include, a) historical CRC Brakleen products all contained less than 1,000 ppm benzene, b) the work simulations involved typical use and worst-case exposure conditions, and c) toluene in Brakleen recipe contains less than 1 ppm benzene. As noted, the authors should have specifically disclosed a) CRC has been a defendant in benzene exposure lawsuits involving Brakleen products, b) Dr. Williams has testified as an expert witness on behalf of CRC in Brakleen lawsuits, and c) their article could be used by CRC in pending and future Brakleen lawsuits. To be taken seriously, in their response the authors should address all the issues I raised, including their implicit claim that toluene used to make commercial Brakleen contains less than 1 ppm benzene. Since the chemical engineering technology for

manufacturing toluene is essentially unchanged for almost a half century, the authors should disclose specific details about any new manufacturing process capable of producing nitration grade toluene - or for that matter any toluene - that has less than 1 ppm benzene.

ACKNOWLEDGMENTS

As a chemical engineer, I am a voting member of three ASTM Committees, including one (D02) that evaluates analytical testing methods for determining the properties of petrochemical products (including benzene content). I have testified opposite Dr. Williams in numerous benzene exposure cases, including at least one involving CRC Industries as a defendant.

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INTRODUCTION

On May 15, 2018, I submitted a letter to the editor of JOEH ("first letter") concerning an "accepted" manuscript entitled *Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work.* For reasons discussed below, I withdrew my first letter and am responding to the revised manuscript that was recently published.[1]

My first letter asserted that the accepted manuscript was scientifically flawed and misleading. In it, I identified two undisclosed conflicts of interest: 1) CRC Industries has been a defendant in benzene exposure lawsuits concerning its Brakleen brake cleaners ("Brakleen"), and 2) one of the authors, Dr. Williams, has testified for CRC Industries regarding the benzene content of Brakleen brake cleaners and benzene exposures arising from their uses." The JOEH editor (R. Anthony, personal communication June 15, 2018) informed me that the authors had been provided my "first letter." In that email she also sent an updated "final" manuscript" (i.e., the published version). The latter has at least seven substantive revisions, with all but one inarguably in response to my first letter. For the reasons presented below, I believe the "final" manuscript remains scientifically flawed and misleading, and hence this second letter.

CONFLICTS OF INTEREST

As they conducted their review of the manuscript, JOEH peer reviewers were unaware of important and undisclosed conflicts of interest. 1) The "final" manuscript does not disclose that one of the authors (AM) has authored numerous published articles in which financial sponsorship came from chemical

manufacturers and chemical trade associations, including the American Chemistry Council and the American Petroleum Institute. 2) The authors acknowledge that CRC "funded the field exposure study." However, their assurance that "no financial support or oversight was provided for the preparation of this manuscript" is inaccurate; namely, the article essentially mirrors an unpublished report, *Workplace/Simulation Study of Benzene and Total Hydrocarbon (THC) Exposures Associated with an Aerosol Brake Cleaner,* dated January 20, 2017 (discussed later in this letter) that was "prepared for CRC Industries" and "led by" AM and PDRW. By "prepared for", I infer that CRC paid for it. 3) The authors do not disclose that the 2017 CRC-funded study has been regularly utilized by CRC and PDRW in benzene exposure lawsuits (it is therefore referred to in this letter as the "litigation study"). 4) The "accepted" manuscript withheld the fact that Dr. Williams has served as an expert witness for CRC. The "final" manuscript only somewhat corrects that oversight. It falls short of disclosing that PDRW has been an expert witness for CRC on at least eight occasions since 2012. Billing records in just one case reveal her charges for time spent in excess of $40,000 - incurred in just two months.

BENZENE AND OTHER CHEMICALS FOUND IN TOLUENE

The refinery process for manufacturing toluene consists of three steps, 1) catalytic reforming, 2) extractive distillation to remove aliphatic impurities, and 3) several distillations to separate toluene from benzene and other aromatics.[(2)] Since catalytic reforming has been widely-used since the 1950s,[(3)] and the process just described has been the same for decades, it is unsurprising that the

benzene content of toluene has remained the same over that same period.[4] Nevertheless, the authors revised the accepted manuscript by implying (without citing a reference) that comparable grades of toluene contained more benzene in the past than now.

Toluene comprised 38.3% of Brakleen Blend A. The grade and provenance of the toluene CRC used is not discussed in the article. Based upon the 1.4 ppm benzene in Blend A that ALS Global measured, Blend A toluene contained only 3.68 ppm benzene. Such an ultrapure toluene (not made in a refinery process) requires complex and expensive treatment that incorporates the drying of purchased toluene with an active reagent, and then distilling it under an inert atmosphere.[5] Sigma Aldrich sells an ultrapure toluene[6] (costing more than $100 per 150 ml septum) that is guaranteed to be more than 99.9% pure and to contain less than 100 ppm benzene - probably a lot less. One expects negligible concentrations of xylene isomers, ethyl benzene, and nonaromatic hydrocarbons to be present in such an ultrapure toluene.

Consensus ASTM specifications exist for the three commercial grades of toluene, (a) industrial[7], (b) nitration[8], and (c) TDI feedstock.[9] TDI feedstock is the *only* toluene grade having specified maximum benzene content (300 ppm). ASTM specifications for the nitration and industrial grades also place no concentration limits on xylene isomers and ethyl benzene. To be discussed is the fact that toluene sold for solvent use (nitration and industrial grades) contains significant concentrations of benzene, xylene isomers (ortho, meta, para), ethyl benzene, and nonaromatic hydrocarbons such as heptane isomers. Table 1

summarizes the benzene content of different grades of toluene. Variability in benzene levels occurs because toluene is a commodity product that is frequently a mixture comprised of toluene coming from different manufacturers and refineries.[4]

CRC uses nitration grade toluene in its Brakleen products.[10] However, based on three factors (and assuming the ALS Global measurements are accurate) I conclude that nitration grade toluene was not used to formulate Brakleen A. First, the 3.68 ppm benzene content of the toluene used in Brakleen A is up to four orders of magnitude below the benzene content of nitration grade toluene. In fact, *Blend A toluene contains less than 0.2% of that found in the unspecified grade of toluene sold by Total Petrochemicals in 2013* (see Table 1). Second, ALS Global did not measure any nonaromatic hydrocarbons in Brakleen A, a result that is inconsistent with the fact that nitration grade toluene is known to contain significant levels of nonaromatic hydrocarbons.[8, 11] Third, Supplemental Table 1 reports *only* the amount of xylene added by CRC to achieve the targeted xylene concentration in Blend A. The results should have also reflected xylene isomers and ethyl benzene known to be present as important contaminants in nitration grade toluene. For example, the concentration of C_8 aromatics (combined xylene isomers and ethyl benzene) in nitration grade toluene can easily exceed 10,000 ppm.[11,12]

CERTIFICATES OF ANALYSIS (COAs)

My first letter pointed out, “The authors, who appear to have blindly accepted the analytical result communicated to them, offer no documentation

(e.g., certificate of analysis, initial boiling point, paraffin content) for the toluene grade used by CRC in formulating the "historical" Brakleen blend A." In response, the authors now state that COAs they reviewed "are consistent" with the benzene contents in Supplemental Table 1. Since the COAs were not cited, it is obvious that they were neither seen nor considered by JOEH peer reviewers. The CRC litigation study does not discuss COAs, or even acknowledge the need demonstrate that reported benzene content for Brakleen blends are accurate and representative of Brakleen non-chlorinated brake cleaners placed in the stream of commerce.

It is widely understood that supplier COAs do not necessarily provide robust and accurate information concerning the composition of raw materials. It is for that reason that scientists recognize the importance of a) independent, third party analytical testing of purchased raw materials, and b) verifying the accuracy of COAs.[13-15] For instance, in discussing the sampling and testing of raw materials, the US Food and Drug Administration (FDA) writes, "As a minimum, a complete analysis should be performed at appropriate intervals and compared with COAs. Reliability of COAs should be checked at regular intervals."[14] Similarly, a well-known analytical chemistry textbook recommends that analytical methods referred to in COAs be "critically reviewed."[15] For reasons explained in the next paragraph, it is quite clear that neither the authors nor CRC can verify the accuracy of benzene contents communicated in toluene COAs utilized by CRC after 2001.

The above admonitions are highly relevant in the present instance because it has been established that errors occur in the reporting of benzene contents in toluene COAs. For example, over a period of many years, a major toluene producer/supplier admitted furnishing COAs in which ASTM D2306[16] was listed as the test used to measure the benzene content of toluene reported in COAs.[17] However, D2306 measures the distribution of ethyl benzene and the three xylene isomers present in *xylene mixtures*. Obviously, since *D2306 has nothing to do with benzene or toluene,* all the benzene contents reported in the toluene COAs issued during the multiyear period were erroneous. As an expert witness for CRC, PDRW prepared *summaries* of approximately 400 COAs for toluene CRC used in its Brakleen products - including at least 52 from the major supplier that used the wrong ASTM analytical testing method, ASTM D2306. "Hundreds" of COAs were also available in late 2014 for toluene and other ingredients CRC used in Brakleen products.[20]

As noted, there is no indication that JOEH peer reviewers considered the relevant COAs in their evaluations - or even saw them. Since the authors relied on them, the COAs in question - <u>not the summaries</u> - should be produced to JOEH. While I had hoped to discuss the COAs in this letter to the editor, I received no responses to my requests that they be provided to me. (A. Selisker, personal communication, May 3, 2018) (V. Henry, personal communication, June 19, 2018)

MISLEADING "SPIKED" BRAKLEEN BLENDS

Brakleen blends B and C were obtained by "spiking" Blend A with pure benzene to achieve "targeted" benzene contents of 100 ppm and 1,000 ppm, respectively. The article thus creates the impression that non-chlorinated Brakleen products in the stream of commerce never contained more than 1,000 ppm benzene (an important threshold in benzene exposure litigation). Given the proportion of toluene in Brakleen Blend A, the authors are also creating the impression that nitration grade toluene cannot contain more than 2,600 ppm benzene, which Table 1 shows is not the case. In order to know how much benzene and toluene to add to the blends to achieve the targeted compositions, CRC would first need to know that the toluene used contained de minimus levels of xylene isomers, ethyl benzene, benzene, and nonaromatic hydrocarbons.

ANALYTICAL RESULTS

It would have been quite easy and straightforward to accurately determine the benzene content of the Brakleen blends. First, the benzene content of the toluene used could have been accurately measured using ASTM International D2360, which has a benzene detection limit of 10 ppm.[21] ASTM testing methods are consensus gold standards[4] that are used to referee disputes.[15] Then, the benzene content of the blend would have been easily calculable by multiplying the ASTM 2360 result by the fraction of the blend that was made up of toluene. Instead of this approach, the "final" article reports that NIOSH NMAM 1501[22] (a peer-reviewed method for air samples only) was used to analyze the Brakleen liquid blends.) Curiously, NMAM 1501 is not mentioned in relevant analytical testing records forwarded to me by JOEH. (JOEH: personal communication, July

3, 2018) Rather, the records reveal that an ALS in house method ("IH-001") was used to analyze Brakleen blends. I have not seen the IH-001 standard operating procedure and am not prepared to comment on it in this letter. The CRC litigation study does not identify a specific test; as with the "accepted" manuscript it says GC/FID was utilized.

The article does not explain a few reporting errors regarding the analysis of bulk Brakleen blends. Supplemental Table 1, which reports the measured composition of bulk Brakleen blends and aerosols, does not account for 58,000 ppm and 28,500 ppm of other chemicals present in the A and C blends, respectively. For the B Blend, the measurements add up to 105.2%. Those errors are significant and must be explained. Additionally, the "final" manuscript does identify the chemicals that comprise "THC" in Supplemental Tables 2, 3, and 4. If only hydrocarbons are included, then the tabulated values are much too *high*, given that the only hydrocarbons said to be present in the Brakleen blends are toluene and small amounts of benzene and xylene. On the other hand, the tabulated values are too *low* if they include airborne acetone and/or methanol, given the physico-chemical properties of both. In the section that concerns the CRC litigation study, reference is made to analytical testing concerns that were communicated to the authors, and that were not carried through to the "final" manuscript.

"TYPICAL" AND "WORST CASE" MISCHARACTERIZATIONS

The assertions that the simulations corresponded to "typical use of an aerosol brake cleaner," and that some high-temperature/low-air-speed conditions

encountered represented “worst-case workplace conditions,” are offered absent independent verification and seem based on the authors’ opinion. The fact is, the authors studied one mechanic in one facility during eight uses of a brake cleaner. I note that “typical” is missing in the title to the CRC litigation study.

To determine “typical use,” one would need to look at the variation in aerosol brake cleaner use by a sizable random sample of mechanics performing the same type of brake job(s). Exposure determinants that pertain to “typical use” are a) the total volume of solvent sprayed per wheel in a specified time period, b) the fraction of sprayed solvent that runs off into a drip basin or onto the floor, c) the temperature of the sprayed surface and aerosol product (which need not be the same as the air temperature), and d) the proportion of the task period (say, 15 minutes) that the mechanic’s face is close to the evaporating solvent and the timing of cleaning. The authors’ report data related to item (a) in their Figure 3, but report no data for items (b)-(d). By the timing of cleaning, I refer to whether the mechanic begins cleaning a surface immediately after spraying it, or whether the mechanic walks away after spraying the surface to perform a different task or to let the solvent act on grime, and then returns to the sprayed surface some minutes later. The former timing would lead to a higher breathing zone solvent exposure intensity compared to the latter timing.

The authors’ assertion that some simulations were performed under “worst-case workplace conditions” is also unfounded. To start with, the authors do not consider environmental conditions and patterns of use encountered by mechanics in countless other workplaces. During the present study, outdoor air

temperatures ranged from 70 to 90 degrees F, and indoor air temperatures ranged from 82 to 96 degrees F. In Phoenix, AZ, the average outdoor high temperature in July is 106 degrees F; without air cooling, the corresponding average indoor high air temperature would be at least 106 degrees F. With regard to air speeds, the speeds depicted in Figure 5(a) appear consistent with the findings of Wilson, et al., (cited as a reference) who reported that "the GM air speed was 3 and 4 m/min (10 to 12 ft/min) in rear and middle work areas" of ten vehicle repair shops. The majority of work stations need not be located at the fronts of shops near open garage doors where air speeds are higher.

Interestingly, the testimony[18] of a CRC Vice President in a lawsuit seems to refute the "typical" and "worst case" exposure characterizations in the article. The testimony was that CRC had never conducted benzene exposure monitoring tests during use of its Brakleen product because: "We wouldn't be able to properly reproduce every possible scenario that a mechanic would encounter. There's so many environmental conditions that need to be measured in any specific test that if we were to test in one area and come up with the results, they would probably not be meaningful to the next person in another scenario."

CRC LITIGATION STUDY

There are noteworthy differences between the CRC litigation study and the "final" manuscript: 1) It has a title different than the article and does not contain the word "typical." 2) Table 1 in the study provides the chemical composition for Brakleen product 05088. I conclude that xylene was present in the commercial product because it was a contaminant in the toluene at 5,222

ppm, consistent with the earlier discussion about xylene levels in nitration grade toluene. 3) The study reports that ALS Global used GC/FID to analyze bulk Brakleen, the same approach the “accepted” manuscript discusses. It makes no mention that NIOSH NMAM 1501 was used for the bulk liquid analyses. As noted, lab records show reveal that in-house method IH-001 test (not offered in the ALS Catalog) was used. 4) The litigation study mentions the ALS Laboratory director raised questions about the identity and concentration of chemicals comprising the THC results. Reference to this unresolved problem was omitted from the “final” manuscript. 5) The “final” manuscript does not repeat the admonition from the same ALS director that ”methanol and acetone (two of the primary constituents of the Brakleen formulations) are not designated analytes per the NIOSH 1501 method.” As discussed earlier, methanol and acetone present potential analytical interferences to NMAM 1501. 6) The “final” manuscript does not communicate the fact that, because of equipment malfunctions, “the air exchange rate in the garage was not measured during the study.” I provided the JOEH editor with documents discussed herein that pertain to the CRC litigation study. (Dr. R. Anthony, personal communication, July 5, 2018)

CONCLUSION

This article communicates inaccurate and misleading results. Based on the many issues raised in this letter, along with the JOEH view that “Short Reports” are articles having “limited generalizability” (JOEH, personal communication, June 15, 2018) the authors should not have offered their opinion that the results are

representative of typical and worst case exposures a mechanic would encounter while using Brakleen products. I recommend an erratum deleting “typical” from the title, and deleting “typical” and “worst case” from the body of the article. I also recommend that in a supplemental on-line file, the authors make available to JOEH readers the unedited toluene Certificates of Analysis (not summaries) upon which they relied. Finally, I recommend that, in the future, JOEH should require authors to provide enough information to allow reviewers to evaluate the accuracy of analytical testing records.

ACKNOWLEDGEMENTS

I am a voting member of three ASTM Committees, including one (D02) that evaluates analytical methods for determining the properties of petrochemical products (including benzene content). I have testified opposite Dr. Williams in numerous benzene exposure cases, including at least one involving CRC Industries as a defendant. I did not serve as an expert witness in any matter in which the CRC litigation study was relevant. I have never received compensation for preparing articles published in peer-reviewed journals.

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Table 1: Benzene Content of Different Toluene Grades

TYPE OF TOLUENE	YEAR	BENZENE CONTENT PPM w/w unless otherwise stated
Blend A Toluene (Note 1)	2018	3.68
Ultra Pure[6] (Note 2)	2018	Up to 100
Hillman (Note 3)	1978	Possibly greater than 1,000
Reference Grade[23] (Note 4)	2002	Up to 1,000 ppm
Nitration[11]	2006	20,000
Nitration[12]	2008	20,000 (up to 50,000)
Nitration[24]	2011	Up to 2.29% (molar)
Unspecified[25]	2013	2,000
Unspecified[26] (Note 5)	2017	Greater than 1,000
Commercial[27] (Note 6)	2000	Up to 25,000
Commercial[28] (Note 6)	2014	Up to 15,000

Note 1: Article does not provide grade and purity
Note 2: Purity guaranteed to be higher than 99.9%; $125 per 150 ml septum
Note 3: Reference #2 in the Article refers to toluene as “benzene critical” solvent
Note 4: Purity higher than 99.9% (per ASTM TDI Feedstock Toluene); MSDS has benzene carcinogenicity warning
Note 5: Toluene is Category 1A carcinogen because it contains more than 1,000 ppm benzene
Note 6: Does not specify if nitration or industrial

Journal of Occupational and Environmental Hygiene

Letter to the Editor regarding "Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work"

Journal:	*Journal of Occupational & Environmental Hygiene*
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INTRODUCTION

The purpose of this letter is to discuss scientific errors, inaccurate statements, and undisclosed conflicts of interest in the Short Report (SR), *Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work.* [(1)]

UNDISCLOSED CONFLICTS OF INTEREST

1) The same authors conducted the CRC-funded simulation in 2016, two years before publication of the SR. The findings and simulation results were memorialized in an unpublished report (available as a supplement to this letter)**.** 2) The unpublished report is utilized regularly in benzene exposures lawsuits, with one of the authors (PDRW) relying on it in as a CRC expert witness in at least two benzene exposure lawsuits, 3) The SR draws extensively from the unpublished litigation report without referring to it, and 4) One of the authors (AM) is the author of numerous published articles funded by chemical manufacturers and chemical trade associations, including the American Chemistry Council and the American Petroleum Institute.

BENZENE CONTENT OF TOLUENE

Consensus ASTM specifications exist for the three commercial grades of toluene, (a) industrial[(2)], (b) nitration[(3)], and (c) TDI feedstock.[(4)] TDI feedstock is the *only* toluene grade having specified maximum benzene content (300 ppm) *and* minimum purity (99.9% toluene). Toluene sold for solvent use (nitration and industrial grades) also contains benzene, xylene isomers (ortho, meta, para), ethyl benzene, water, and nonaromatic hydrocarbon impurities such as heptane

isomers. Variability in composition occurs because toluene is a commodity product that is frequently a mixture comprised of toluene from different manufacturers and refineries.[5] The refinery process for manufacturing toluene consists of three steps, 1) catalytic reforming (widely used since the 1960s[6]), 2) extractive distillation to remove aliphatic impurities, and 3) several distillations to separate toluene from benzene and other aromatics.[7] Since the process just described has been the same for decades, it is unsurprising that the benzene content of the different grades of toluene has remained the same over that same period.[5] Table 1 summarizes the benzene content toluene prior to 2013. ASTM specifications for *nitration grade* toluene became more stringent in 2013 (minimum purity of 98.8%; but no limit on benzene content).[8]

Brakleen Blend A contained 38.3% toluene. Since the measured benzene content of Blend A was reportedly 1.4 ppm, the toluene that CRC used to prepare it contained only 3.66 ppm benzene (1.4 /0.383). This benzene content is to be viewed with skepticism because, with the exception of ultrapure toluene used in laboratory applications, it is orders of magnitude below the benzene levels in Table 1 (spanning 1978 to 2017). Each order of magnitude is a factor of ten.

"SPIKED" BRAKLEEN BLENDS

CRC prepared Brakleen blends B and C by "spiking" Blend A with pure benzene to achieve "targeted" benzene contents of 100 ppm and 1,000 ppm, respectively. This creates the impressions that a) non-chlorinated Brakleen products could not contain more than 1,000 ppm benzene (an important

threshold in benzene exposure litigation), and b) toluene cannot contain more than 2,600 ppm benzene (1,000/0.383), which Table 1 shows is not the case. The grade and benzene content of toluene that CRC used to prepare Blend A was not mentioned in the Short Report. Without first testing for the benzene content of Blend A toluene, CRC could not have known the volume of benzene necessary to achieve the "spiked" benzene contents - unless the toluene used contained almost no benzene (consistent with an ultrapure toluene sold for laboratory applications). CRC does not test to determine the benzene content of incoming toluene.[9]

RELIABLE WAY TO DETERMINE BENZENE CONTENT OF CRC BLENDS

The benzene content of the CRC Brakleen blends could have been reliably determined by using a widely accepted standard method that has undergone peer review. First, the benzene content of the toluene used in the blends could have been accurately measured using ASTM International D2360, which has a benzene detection limit of 10 ppm.[10] The benzene content of Blend A is calculable by multiplying the ASTM 2360 result by the fraction of the blend that was made up of toluene. ASTM testing methods are consensus standards that are used to referee disputes.[11] As discussed below, the accuracy and reliability of the reported benzene contents of CRC blends are very much in question.

ANALYTICAL TESTING OF BULK LIQUID BRAKLEEN BLENDS

There appears to be a difference of opinion between the authors and ALS Global regarding the analytical testing method used to measure the benzene

content of bulk Brakleen blends. According to the SR, ALS analyzed the liquid blends by NMAM 1501[12] with an Agilent DB-MTBE capillary column. According to ALS, however, it used testing method "Gas-Chromatography-Rinsate IH-001" (not offered in the ALS Catalog of services) - not NMAM1501 as stated by the authors. "IH" can denote an in-house test. Finally, the aforementioned unpublished report (available as a supplement to this letter) states the Brakleen blends were analyzed by gas chromatography with a flame ionization detector (no specific analytical testing method was identified). The scientific merit of the reported benzene contents cannot be established without identification of the actual analytical testing method and its performance properties (e.g., detection limit, precision, reporting limits, interferences). The article does not say if the "IH" test has been published or peer-reviewed, or if it represents a modification of NMAM 1501. In general, it is a good idea for authors to communicate details about unpublished analytical methods, as well as about standard methods that have been modified, so reviewers and readers can better understand the method and evaluate the results. It is unclear why the authors selected a laboratory that they say is accredited to perform NMAM 1501 on *air samples*, while at the same time acknowledging that the lab lacks accreditation for determining the benzene content of bulk liquids.

There are legitimate concerns if NMAM 1501 was used to analyze liquid samples. To start with, the capillary column identified by the authors differs markedly from the one specified in NMAM documentation (fused silica PEG capillary column or equivalent having *polar* properties). The column discussed in

the SR, Agilent DB-MTBE, is a *non-polar* column for determining the concentration of MTBE in *soil and water*. Secondly, NMAM 1501 is for determining the concentration of aromatic hydrocarbons in *air samples*. It is not intended for liquids. Lastly, ketones and alcohol (which comprise more than 60% of the Brakleen blends) are known to present potential analytical interference with NMAM 1501 determinations.

"TYPICAL" AND "WORST CASE" MISCHARACTERIZATIONS

Because Short Reports have limited generalizability, the authors should not have offered their opinion that the results are representative of typical and worst case exposures that a mechanic would encounter while using Brakleen products. The assertions that the simulations corresponded to "typical use of an aerosol brake cleaner," and that some high-temperature/low-air-speed conditions encountered represented "worst-case workplace conditions," are offered absent independent verification and seem based on the authors' opinion. The fact is the authors studied one mechanic in one facility during eight uses of a brake cleaner.

The assertions are unfounded because the authors do not consider environmental conditions and patterns of use encountered by mechanics in countless other workplaces. The fact is that benzene exposures are known to occur under widely different conditions. To this point, CRC has not monitored benzene exposure during the use of Brakleen products because: "We wouldn't be able to properly reproduce every possible scenario that a mechanic would encounter. There's so many environmental conditions that need to be measured in any specific test that if we were to test in one area and come up with the

results, they would probably not be meaningful to the next person in another scenario." [12]

CONCLUSION

Because this Short Report communicates inaccurate and misleading findings, it is recommended that readers exercise caution in interpreting and applying the results.

ACKNOWLEDGEMENTS

I am a voting member of three ASTM Committees, including one (D02) that evaluates analytical methods for determining the properties of petrochemical products (including benzene content). I have testified opposite Dr. Williams in numerous benzene exposure cases, including at least one involving CRC Industries as a defendant. I recently learned that Dr. Williams is an expert witness in a benzene exposure case involving the use of a non-chlorinated brake cleaner in which I am an expert witness for the other side. I have never received compensation for preparing published articles.

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Table 1: Benzene Content of Different Toluene Grades

TYPE OF TOLUENE	YEAR	BENZENE CONTENT PPM w/w unless otherwise stated
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Ultra Pure[13] (Note 2)	2018	Up to 100
Hillman (Note 3)	1978	Can be greater than 1,000
Reference Grade[14] (Note 4)	2002	Up to 1,000 ppm
Nitration[15] (Note 5)	2006	20,000
Nitration[16] (Note 5)	2008	20,000 (up to 50,000)
Nitration[17] (Note 5)	2011	Up to 2.29% (molar)
Unspecified[18]	2013	2,000
Unspecified[19] (Note 6)	2017	Greater than 1,000
Commercial[20] (Note 7)	2000	Up to 25,000
Commercial[21] (Note 7)	2014	Up to 15,000

Note 1: CRC never performed analytical testing to measure the amount of benzene in incoming shipments of toluene used in Brakleen.[12]
Note 2: Purity guaranteed to be higher than 99.9%; $125 per 150 ml septum
Note 3: Reference #2 in the Short Report refers to toluene as a "benzene critical" solvent that has "typically presented problems because it can contain relatively high benzene contents (greater than 0.1 percent benzene)."
Note 4: Purity higher than 99.9% (per ASTM TDI Feedstock Toluene); MSDS has benzene carcinogenicity warning.
Note 5: In 2013 ASTM established a minimum purity specification (98.8%) for nitration grade toluene - no maximum benzene specification[8]
Note 6: Document discloses that toluene is a Category 1A carcinogen because it contains more than 1,000 ppm benzene
Note 7: Does not specify whether nitration or industrial grade (both grades are used as solvents).

Journal of Occupational and Environmental Hygiene

Letter to the Editor regarding "Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work"

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Letter to the Editor regarding "Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work"

Key Words: Benzene exposure; brake cleaner; industry funded; toluene

Exposition Word Count: 1,614

INTRODUCTION

In this letter I discuss scientific errors, inaccurate statements, and undisclosed conflicts of interest in the Short Report (SR), *Airborne exposures associated with the typical use of an aerosol brake cleaner during vehicle repair work.* [1] Letters to the Editor and Commentaries augment the peer review process by providing important checks and balances to help ensure that results reported in published articles have scientific merit. In this regard, I previously commented on another benzene exposure article in a letter to the editor.[2] More recently, I critiqued the occupational exposure section of the most recent IARC Benzene Monograph in a published Commentary.[3] Others have done so as well.[4, 5]

Undisclosed Conflicts of Interest

The authors do not reference an unpublished benzene exposure report[6] ("CRC report" dated January 20,2017). Nor do they disclose that conclusions, figures, and tables offered in the SR come directly from that report. I believe the "in-field exposure study" of August 4-5, 2016, and the CRC report that followed a few months later, were not exercises in academic research. They pertained to benzene exposure litigation involving the sponsor, CRC Industries. The SR does not disclose the fact that as a testifying expert for CRC, one of the authors (PDRW) referenced the CRC report in at least two court

cases (Simmons[7] and Pennington[8]) to buttress her opinions about benzene exposures arising from non-chlorinated Brakleen products.

The SR Draws Heavily from the CRC Report

SR analytical results were first presented in the CRC report. Figures and tables in the SR were directly constructed from tabulated results in the CRC report. Three ALS Laboratory ("ALS") reports[9] (all dated August 11, 2016) reflect results from ALS analytical testing of bulk Brakleen samples received from PDRW on July 18, 2016. The ALS-determined compositions of Brakleen blends are tabulated in Appendix 2 of the CRC report and in Supplemental Table 1 of the SR. The SR refers to 104 charcoal samples collected during the "in-field exposure study" - the same number of airborne samples for which analytical results are provided in Appendix 3 of the CRC report. Supplemental Tables 2, 3, and 4, as well as Figure 2, of the SR are constructed directly from the 104 tabulated results in Appendix 3 of the CRC report. They are identical in terms of amount of product used and measured airborne concentrations. The only difference is that Appendix 3 of the CRC report tabulates 104 airborne benzene levels below the detection limit, while the published article consolidates the same results in a sentence on page 534, "Benzene was not detected in any of the personal, area, and background samples at a detection limit of approximately 0.3 mg/mg^3 (0.1 ppm)."

ANALYTICAL TESTING OF BULK LIQUID BRAKLEEN BLENDS

The authors report that ALS analyzed the bulk blends using "*the same analytical method and quality control procedures as for the charcoal air samples*." (Emphasis added) More specifically, the authors inform readers that air samples (and thus the bulk blends as well) were analyzed by NIOSH 1501 (which is applicable to air samples only). I note that the

Agilent DB-MTBE capillary column discussed in the SR is applicable to MTBE in soil and water matrices.[10]

The three ALS reports identify "Gas-Chromatography-Rinsate IH-001" ("IH-001") as the method used to analyze the bulk Brakleen blends, and indicate that chain of custody seals were not present for sample bottles and shipping containers received from E Risk Science. Method IH-001 (not offered in the ALS Test Catalog and Fee Schedule[11]) appears to be an in-house test whose performance properties (e.g., detection limit, precision, reporting limits, interferences) have not been peer-reviewed. In general, it is a good idea for authors to communicate details about unpublished analytical methods, as well as about standard methods that have been modified, so reviewers and readers can better understand the method and evaluate the results.

Of additional concern is the fact that ketones and alcohols (which comprise more than 60% of the Blend A standard) are known to present potential interferences with NMAM 1501 determinations. This important concern is not referred to in the SR, but is acknowledged in the CRC report, "Note that methanol and acetone (two of the primary constituents of the Brakleen® formulations) are not designated analytes per the NIOSH 1501 method." It is unclear why the authors did not request ALS to analyze air samples by OSHA Method 12 (offered in the ALS catalog) and for which there are minimal interferences.

Curiously, the authors acknowledge that ALS is unaccredited to perform bulk sample analyses. That lack of accreditation is certainly not ALS's fault. The authors - or CRC Industries - should have engaged a laboratory accredited in ASTM D7504[12] to

determine the benzene content of toluene used to formulate the Blend A, after which the Blend A benzene content could have been accurately calculated.

Benzene Content of the Blend a Standard and Toluene

For the "in field exposure study", CRC prepared a Blend A standard to replicate the recipe for a historical Brakleen product (sold between 1999 and 2011 according to the CRC report): toluene (38.3%), methanol (35.5%, acetone (19.5%), CO_2 (6.5%), and xylene (0.2%). The authors claim their reported benzene content for Blend A (1.4 ppm) is "consistent with current supplier certificates of analysis [COAs] for the main hydrocarbon ingredient (toluene), but which do not necessarily reflect historical levels." The COAs are not identified, and will be discussed further. The suggestion that current benzene levels in toluene are lower than in the past is incorrect because the refinery process for making toluene is unchanged for at least fifty years; catalytic reforming, followed by extraction to remove aliphatic chemicals, followed by distillation.

More importantly, the reported 1.4 ppm benzene content of Blend A would require the toluene to contain only 3.66 ppm benzene. The latter is consistent with a laboratory-grade reagent, which is far too expensive for use in a commercial solvent cleaner. Even ultrapure (>99.9%) TDI-grade toluene[13] may contain 300 ppm benzene (up to 82-fold more than in Blend A toluene). In fact, CRC has historically used a far less pure toluene (nitration-grade) to manufacture Brakleen products; nitration-grade toluene[14, 15] has never had a benzene specification, and until 2013 had no minimum purity requirement. The prospect that toluene used in commercial Brakleen products contains only 3.66 ppm benzene, at present and/or in the past, is highly improbable.

For the "in field exposure study", CRC is said to have "spiked" Blend A with pure

benzene to achieve "targeted" benzene contents of 100 ppm (Blend B) and 1,000 ppm (Blend C). This exercise intimates that historic Brakleen (which is the subject of many benzene exposure lawsuits) contained no more than 1,000 ppm benzene (an important threshold in benzene exposure litigation). The 1,000 ppm value does not comport with two results for non-chlorinated carburetor cleaners (known to have formulations similar to brake cleaners) reported in SR reference #5. The first was a carburetor cleaner formulated with toluene, methanol, and acetone (ID#525308 in the study) found to contain 9,000 ppm benzene. Because it comprised only a fraction of the product, the toluene used certainly contained well in excess of 10,000 ppm benzene - consistent with benzene contents for toluene reported in two of my published articles[16, 17]. The second carburetor cleaner (ID#225108 in the study) contained 2,000 ppm benzene. I note that all but one of the brake cleaners in the study (including a CRC Brakleen product) were *chlorinated*, and therefore not expected to contain much benzene.

Certificates of Analysis

Verifying the accuracy of COAs, and the importance of independent, third party analytical testing of purchased raw materials, are widely understood to be very important[18]. A well known gas chromatography textbook warns that analytical methods referred to in COAs should be "critically reviewed."[19] To this point, in discussing the sampling and testing of raw materials, the US Food and Drug Administration (FDA) writes, "As a minimum, a complete analysis should be performed at appropriate intervals and compared with COAs. Reliability of COAs should be checked at regular intervals." [20] A topical example underscores why it is bad practice to accept unverified COAs as valid laboratory records. A major manufacturer and distributor of toluene produced

COAs in which ASTM D2306[21] was listed as the analytical test used to measure benzene content (some of the COAs actually reported a benzene content of 0.0 ppm) even though the test has nothing at all to do with assaying benzene in toluene (it determines the distribution of ethyl benzene and three xylene isomers present in *xylene mixtures*). Because COAs do not represent laboratory records, and because the authors cannot confirm the accuracy of their unreferenced toluene COAs, it was improper of them to suggest they corroborate the reported result that the Blend A standard contained 1.4 ppm benzene.

"Typical" and "Worst Case" Mischaracterizations

Short Reports "should acknowledge that the findings might only apply to the limited sites/conditions included in the study" because they present "a relatively small number of measurements."[22] In this instance, the authors studied just one mechanic in one facility during eight uses of a brake cleaner. The authors readily acknowledge a "paucity of data" and a "limited dataset" on benzene exposures arising from the use of aerosolized non-chlorinated brake cleaners. Based on these circumstances, the conclusions offered by the authors that the results are representative of "typical" and "worst case" exposures a mechanic would encounter are inappropriate and misleading. They seem based on the authors' opinion and are offered absent independent verification.

CONCLUSION

Because this Short Report communicates inaccurate and misleading findings, it is recommended that readers exercise caution in interpreting and applying the results. Documents not available to the public (e.g., COAs; SOP for IH-001) should be cited and produced to the journal.

ACKNOWLEDGMENTS

I am a voting member of three ASTM Committees, including one (D02) that evaluates analytical methods for determining the properties of petrochemical products (including benzene content). As a chemical engineer, I testify on behalf of workers who were exposed to brake cleaners and other benzene-containing products. Almost thirteen years ago I neglected to disclose this in a published article.[23] I have testified opposite Dr. Williams in at least one case in which CRC was a defendant, and in a current lawsuit (involving the use of a non-chlorinated brake cleaner) in which Dr. Williams formerly served as an expert witness. I have never received compensation for preparing published articles.

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