Potential risk of benzene in petroleum-derived products used from 1974 to 2012 in Korea

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Abstract

This study was conducted to assess benzene contents in petroleum-derived products (PDPs) through literature reviews reported in Korea, and also to estimate inhalable exposure to benzene of workers handling PDPs that contain trace amounts of benzene. All available data on the benzene-containing products in Korea until 2012 were collected from prior studies, reports and epidemiological surveys. A total of 32 products of 7 reagents, including ethylbenzene and trichloroethylene were also analyzed using a gas chromatograph equipped with a mass spectrometer to confirm the trace levels of benzene. Finally, a total of 112 data set with 131 bulk samples for benzene content information were collected. Thinner had the highest benzene content of 56.7% in 1997, followed by 30.1% for printing agent in 2005, 8.96% for solvent used at maintenance and repair services of motor vehicles in 2005, and 6.0% for gasoline in 2002. The amount of benzene contained in the PDPs showed a declining trend by years, but workers treated with thinners containing less than 0.1% benzene were found to be exposed to concentrations above 1 ppm. Thirteen of the 32 reagents were also confirmed to contain benzene, while the products of trichlorethylene and ethylbenzene contained more than 0.1% benzene. In conclusion, even if the benzene content is below 0.1%, if there is a possibility of benzene exposure, it is warranted to specify presence of benzene in the material safety data sheet to ensure protection of health of workers handling the PDPs.

***Keywords*: Benzene, Petroleum-derived product, MSDS, Reagent**

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Introduction

Benzene is a natural ingredient of crude oil and therefore has been used in various chemical products derived from petroleum, it is used as an ingredient of printing ink, organic solvent, raw material and intermediate in diverse pharmaceutical and chemical industries (e.g., rubber, lubricating oil, dye, detergent, pesticide manufacturing) and an additive in unleaded gasoline (Williams et al., 2008; ATSDR, 2007).

The International Agency for Research on Cancer (IARC) classified benzene as carcinogenic to humans (Group 1) and reported that there is sufficient evidence of benzene's carcinogenicity in acute myeloid leukemia (AML) and acute non-lymphocytic leukemia (ANLL), and a positive association in acute lymphocytic leukemia (ALL), chronic lymphocytic leukemia (CLL), multiple myeloma and non-Hodgkin lymphoma (IARC, 2012). In line with recognition of benzene as a carcinogen, the American Conference of Governmental Industrial Hygienists (ACGIH) lowered its airborne time weighted average (TWA) threshold limit value (TLV) to 0.5 ppm in 1990 (ACGIH, 2001), and the Ministry of Employment and Labor in Korea also reduced the exposure criterion from 1 ppm to 0.5 ppm in 2016 (MOEL, 2016).

Even after the acknowledgement of its hazard, benzene is still included in petroleum-derived products (PDPs) not because it is used for a specific purpose but it persists as an impurity (Kopstein, 2006). It is not only technically challenging to eliminate benzene remaining as an impurity but is also expensive to improve the impurity removal efficiency. As such benzene is not fully eliminated but still continues to be included in petrochemical products used for industrial purposes. Therefore, it is warranted that the Material Safety Data Sheet (MSDS) of petrochemical products must provide clear information on inclusion of benzene in such products.. Under the current Occupational Safety and Health Act in Korea (OSHAct), a presence of a carcinogen should be specified in the MSDS when it represents 0.1% or higher in the mixture (MOEL, 2013).

However, it has been argued that in practice, unlike regulations, benzene is often not included in MSDSs if the content is less than 0.1%, resulting in potential exposures of workers handling petrochemical products without recognizing the presence of benzene (Kopstein, 2006).

Among 34 cases of hematopoietic diseases from 1992 to 2000 claimed in Korea, eight cases were accepted as those related to benzene exposure and included degreasing (four cases), painting (two cases), and gluing (two cases). A case of a worker of CLL who used 100% benzene as degreasing solvent at a telecommunication company was upheld by the court (Kang et al., 2005). In 2012, the Occupational Safety & Health Research Institute (OSHRI) of Korea Occupational Safety and Health Agency (KOSHA) reported ALL of solvent-handling workers in the tire manufacturing business, ALL of thinner-handling workers in truck manufacturing, AML in gasoline-handling workers in vehicle manufacturing, and myelodysplastic syndrome in workers using printed circuit board pre-treatment and plating chemicals in the printing industry and benzene, that may have been included at a trace amount, was suspected as the occupational cause of leukemia (OSHRI, 2012). Nevertheless, currently there are not many investigations on benzene content in domestically available petrochemical products and also assessments of potential exposures to workers handling petrochemicals. The benzene data in the PDPs reported in the published literature written in English language are reviewed by Williams et al. in 2008. However, the amount of benzene in the PDPs actually used in Korea has not been reported.

Against this background, the objectives of this article are (a) to review how many benzene-containing PDPs have been used in Korea; (b) to estimate inhalable benzene exposure level of workers handling benzene-containing PDPs based on the benzene exposure data reported in literatures, and (c) to demonstrate that the highly refined reagents can still contain benzene over 0.1% by weight even when the MSDS doesn't list benzene as an ingredient.

METHODS

Literature search and data analysis

All available data on benzene-containing products existing in Korea until 2012 were collected from prior studies, reports, and epidemiological surveys using the 'Research Information Sharing Service (RISS: http://www.riss.kr)' operated by the Korea Education & Research Information Service (KERIS). For benzene-related literatures, search terms of 'benzene', 'benzene containing', 'benzene including', 'benzene containing substance', 'benzene organic solvent', 'benzene printing', 'benzene paint', 'benzene gasoline' and 'benzene thinner' were used singly or in combination in the RISS. Additional epidemiological survey reports conducted between 1997 and 2012 by the OSHRI under the ISHA were selected as they provided benzene contents. All data were organized by setting the content as 0.1% for data reported as '> 0.1%'.

A total of 128 published literatures were collected, of which 8 (Kim et al., 2006; Lee et al., 2003; Roh et al., 2001; Song et al., 2000; Paik et al., 1998; Shin, 1995; Lee et al., 1990; Ro, 1975) were used as they provided benzene content information. In addition, we selected data from 43 cases reporting benzene content out of 114 unpublished epidemiological survey reports (OSHRI, 2013) conducted between 1997 and 2012 by the OSHRI under the OSHAct. Finally, a total of 112 data set with 131 bulk samples for benzene content information were analyzed by product types. The benzene data contained in the PDPs are summarized in terms of the sample analysis year, PDPs used industry, PDPs type, analysis method and content calculation method (weight ratio, volume ratio, etc.). If there is no information on the sample analysis year, it is replaced with the publication year.

We used the arithmetic mean (AM) as a representative value for analysis of measurements, as the best summary measure of exposure for epidemiologic studies of chronic disease (Seixas et al., 1998). If only the number of measurements and either the geometric mean (GM) and geometric standard deviation (GSD) was provided, a lognormal distribution was assumed and the formula (1) was used to provide an estimate of AM (Aitchison and Brown, 1963).

$$AM = GM \times \exp[1/2 \times (\ln(GSD))^2] \text{ ------------------- } (1)$$

For the benzene content presented with a minimum-maximum range, the AM was calculated with the equation (2) by assuming a lognormal distribution according to the following method: first, the midpoint of the log transformed minimum and maximum values provided an estimate of the mean of the log-transformed levels ($\widehat{\mu_L}$); second, the difference between log-transformed minimum and maximum were divided by four as an estimate of the standard deviation of the log-transformed levels ($\widehat{\sigma_L}$); and finally, AM was calculated using following formula (2):

$$AM = \exp[\widehat{\mu_L} + 1/2 \times \widehat{\sigma_L}^2] \text{ ------------------------------- } (2)$$

When analyzing data collected based on different numbers (N) of observations, it is appropriate to weight each average by a weight that is proportional to the inverse of the variance of the mean (Park et al., 2009). Because we did not have variance estimates, weighted arithmetic means (WAMs) were calculated with the formula (3).

$$WAM = (N_1 \times AM_1 + N_2 \times AM_2 + \cdots + N_n \times AM_n)/N_t \text{ --- } (3)$$

Bulk analysis of benzene contents in reagents with high purity

On the basis of literature review (Williams et al., 2008; Kopstein, 2006; Fedoruk et al., 2003), reagents that are likely to contain benzene were chosen, such as n-hexane, n-heptane, cyclohexane, ethylbenzene, toluene, trichloroethylene and xylene. There are two reasons for selecting reagents to confirm benzene contents in PDPs: first, as reagents have higher purity than industrial-grade products, if benzene is detected in reagents, it can be argued based on this conservative approach that industrial-grade products would have higher contents, and second, as this study is targeting products containing trace amounts of benzene, reagents were chosen as their higher purity would provide lower benzene contents than in industrial-grade items.

To investigate the difference according to manufacturing year, products with the earliest to the latest manufacturing dates were collected among reagents that are commercially available in Korea. The difference according to country of origin and manufacturer was also examined. Finally, a total of 32 reagents manufactured from 2004 to 2013 were collected. MSDSs and labeling information of reagents were also collected to compare the results of analysis. If an MSDS has not been provided along with a reagent, it was obtained by inquiring to the manufacturer or supplier.

For the bulk sample analysis, 1-μL aliquots of the samples were directly injected into gas chromatograph (GC) equipped with a mass spectrometer (Turbo Mass Gold, Perkin Elmer, Norwalk, CT, USA) for analysis of benzene content (weight) in reagents (weight). The temperature of the GC capillary column (60 m x 0.25 mm x 1.0 ㎛, VB-1, Valco Instruments Co. Inc.) was kept at 40℃ for 5 min, and then ramped to 250℃ at a rate of 4℃ min^{-1}, 5℃ min^{-1}, and 20℃ min^{-1} with a final hold of 1 min. The temperatures of the injection port and detector were maintained at 200 ℃ and 250 ℃, respectively. The flow rate of the carrier gas helium (purity of 99.999%) was 1.5 mL/min. Mass range was scanned from 35 to 350 atomic mass unit through selected ion recording mode. The limit of detection (LoD) for benzene (Sigma-Aldrich, HPLC grade ≥99.9%) was 0.005 mg/L.

RESULTS

Content of benzene in PDPs used from 1975 to 2012 in Korea

From literature review, a total of 112 data set with benzene contents were found and detailed information was listed in an Appendix A. The distribution of benzene contents in each product between 1974 and 2012 were summarized in Table. 1.

In terms of number of bulk samples, thinner accounted for the largest proportion of retrieved data (n=51), followed by coating materials (n=23), gasoline (n=15), solvent (n=12), diluent (n=8) and adhesive (n=4). Although the number of samples was small, information on the benzene content in cleaning products, hardener, ink, printing agent, raw material, accelerant, anti-rusting oil, ethyl benzene, fuel, toluene and waste was also collected.

In terms of the maximum benzene content in each product, the highest level was reported for thinner, up to 56.7% (v/v). Thinner also showed the widest content distribution, ranging between 0.00018% and 56.7%. Of products used prior to 1980, only thinner was reported that WAM benzene content was 12.6% and among products used from 1981 to 1999 and after 2000, all but diluent had a mean over 0.1%.

In PDPs used after 2000, both the minimum and maximum benzene contents exceeded the MSDS carcinogenicity listing criterion of 0.1% for adhesive (minimum: 0.13%, maximum: 5.7%), cleaning products (0.17%, 1.5%), raw material (1.1%, 10%) and solvent (0.5%, 8.96%).

Comparison between bulk content and airborne concentration of benzene

We compared the data which have both information of bulk content and exposure level of benzene to workers' handling those products (Table 2).

Ro (1975) reported that 14 thinner products used for dilution or washing contained benzene at 12.6% on average and measured airborne concentrations in two painting workplaces using these products. Workplace A had a local exhaustive ventilation (LEV) system with two horse power (HP) in 85 ㎡ and workplace B had one LEV with three HP and three LEVs with two HP in

92 ㎡. Airborne samples were analyzed with ultraviolet spectroscopy and reported as mean 30 ppm in workplace A and 10 ppm in workplace B.

Song et al. (2000) measured benzene contents in gasoline and airborne exposure concentrations for fuel-filling workers in 7 gas stations in downtown areas and highway rest stops. Airborne concentrations were measured with low-flow pumps and charcoal tubes and analyzed with the gas chromatograph-flame ionization detector (GC-FID). Samples were collected for each of 2 work shifts (7:00-15:00, 15:00-22:00). Area samplers were placed on top of oil supply machines. Personal sampling results ranged between 0.003 ppm and 0.2 ppm, and area sampling measurements ranged between 0.004 ppm and 0.31 ppm. Volatile ingredients including benzene of gasoline bulk samples used in gas stations were also analyzed with GC-FID and found to contain benzene between 2.1% and 5.9%.

According to a study by Roh et al. (2001), benzene was detected at 1.28% in one organic solvent used for dry cleaning and partial stain removal in 20 laundries. Airborne concentrations were measured with low-flow pumps and charcoal tubes and sampling was conducted for 6 or more hours on days when dry cleaning took place. Samples were collected around workers' breathing zone, workstations and washing machines, and analyzed with GC-FID. From personal sampling, the arithmetic mean concentration was 1.43 ppm and from area sampling, the arithmetic mean airborne concentration was 1.19 ppm around workstations and 1.48 ppm around dry cleaning machines.

From an epidemiological survey in a tire manufacturing factory (OSHRI, 2013), a solvent spray solution used in an extrusion division was analyzed with GC-MS and benzene contents in evaporated ingredients ranged between 0.32% and 0.40%. Work environment was monitored for the entire 3-shift workers and samples were collected using low-flow pumps and charcoal tubes. Short-term benzene exposure concentration during a mixing operation was 2.16 ppm and personal sampling results from 14 workers ranged between 0.31 ppm and 0.84 ppm.

In a synthetic leather manufacturing factory, coating materials, solvent, catalyst and hardener were analyzed with GC-MS, and found to contain benzene between 0.7% and 2.0% (OSHRI, 2013). Airborne concentrations were measured in July with a relatively high evaporation rate of benzene, and at the time of monitoring, only an afternoon shift was taking place due to a reduced workload than usual days. Airborne exposure concentrations ranged between 0.02 ppm and 0.05 ppm.

In an epidemiological survey in a vehicle manufacturing factory (OSHRI, 2013), the benzene content in gasoline used in vehicle instrument cluster development testing was 4% according to the product specification. Vehicle instrument cluster refer to the instrument cluster which collects various information about the car such as speed, rotation per minute (RPM), fuel quantity, coolant temperature gauge, etc. at a glance. During development testing of vehicle instrument cluster, personal sampling results in 2 workers ranged between 3.5 ppm and 6.68 ppm. Area sampling measurements ranged between 2.67 ppm and 4.0 ppm.

In an epidemiological survey in a speaker cone paper manufacturing factory (OSHRI, 2013), benzene contents in adhesive bond and airborne benzene exposure concentrations during working hours were measured. Bond ingredients were analyzed with GC-MS, and detected benzene in the bond used for kit bonding and lacquer bonding was at 0.13% and 5.66%, respectively. Airborne concentrations were measured with charcoal tubes near a worker's breathing zone and on workstations close to the worker's respiratory system. Eight-hour weighted mean airborne concentration was 0.05 ppm for kit bonding and lead wire insertion, and the area sampling result at the kit bonding place and the area between lacquer spraying and kit bonding was 0.05 ppm and 0.06 ppm, respectively. There was no ventilation system in the workplace.

In epidemiological survey conducted by KOSHA (OSHRI, 2013) at a painting factory, benzene was detected at 0.01% and 0.05% in two samples of used paints, and airborne concentrations ranged between 0.01 ppm and 6.55 ppm for block painting at a dock and operations inside a ship and in a painting shop.

KOSHA (OSHRI, 2013) monitored a raw material filling operation in a lubricating oil production factory and reported that the airborne exposure concentrations of the main worker who personally observed the filling and a supportive worker were 0.43 ppm and 0.31 ppm, respectively. Sampling was conducted for a 2-hr work shift as the filling operation takes about 2 hours and occurs approximately once every 2 months. The lubricating oil was analyzed and found to contain benzene at 1.1%.

Confirmation of benzene content in reagents

A total of 32 products of 7 reagents, including cyclohexane, ethylbenzene, n-heptane, n-hexane, toluene, trichloroethylene and xylene were analyzed to confirm the trace level of benzene.

Table 3 shows the summary of the results of benzene analyses in 32 bulk samples. Benzene was detected in 13 products of 6 reagent chemicals except in n-heptane products. Maximum benzene content was 0.166% in trichloroethylene, followed by 0.146% in ethylbenzene, 0.064% in toluene, 0.009% in xylene and 0.004% in n-hexane. In some of ethylbenzene (R-8, R-9) and trichloroethylene (R-28) reagents with detected benzene, the level exceeded the MSDS carcinogenicity listing criterion of 0.1%. However, no reagents had benzene information listed in MSDS or labeling as an ingredient.

DISCUSSION

In Korea, domestic benzene production has steadily increased from 1.28 million tonnes in 1995 to 3.23 million tonnes in 2012. Benzene is mainly used as raw materials for styrene monomer, phenol, cyclohexane, aniline, maleic anhydride, and alkylbenzene (KPIA, 2012). Benzene could be also contained as impurities in PDPs such as cleaning agents, adhesives and thinners, which are mainly used in the workplace. However, these products often do not provide benzene information in the MSDS. Therefore, this study attempts to collect as much reported data as possible on benzene content in PDPs used in Korea.

Based on the Korean domestic data collection, thinner had the highest benzene content of 56.7% in 1997, followed by 30.1% for printing agent in 2005, 8.96% for solvents used at maintenance and repair services of motor vehicles in 2005, and 6.0% for gasoline in 2002 (Table 1). The results of this study showed that Korean PDPs contain more benzene contents than the data reported by Wlliams et al. (2008). Williams et al. (2008) reviewed the benzene content data of PDPs reported in the literature from 1956 to 2003. According to their report, the benzene content of petroleum naphthas and other solvents sometimes used in the rubber coating industry was found to equal or exceed 1% in the mid-1950s and early 1960s, with benzene concentrations as high at 9% measured for some naphtha solvents. Hexane, heptane, rubber solvents, lacquer diluents, and toluene also typically contained benzene concentrations at or above 0.1% v/v prior to 1978. However, the benzene content of PDPs declined significantly after the late 1970s and early 1980s and is currently <0.1% v/v for most commercial products.

Among the 112 data points, the data on thinner products was the largest 51, and the content of benzene showed a wide range from 0.00018% to 56.7%. The level of benzene content in the thinner product showed different characteristics depending on the type of thinner. Table 4 compares the results of four studies that report the amount of benzene contained in the thinner according to the type of thinner. Ro (1975) analyzed the benzene content among the 14 thinner products sold in 1974, but no information on thinner types was reported. It is reported that the cause of benzene in thinner is the impurity of industrial toluene, which is the main ingredient in thinner. The benzene and toluene concentrations in each thinner reported in Ro's study are positively correlated (R=0.68) as shown in Fig. 1, and benzene can be estimated to be about 28% of the toluene content. Paik et al. (1998) reported that toluene is the most commonly detected substance in thinners and benzene is not detected in automotive paint thinners. Instead of benzene, xylene, toluene, cellosolve acetate, butyl cellosolve and butyl acetate were frequently detected in automotive paint thinners in Paik's study. In fact, Lee et al. (2003) visited 7 automobile manufacturers and collected 70 paint thinners used in painting process and analyzed their benzene content. As a result, it was reported that trace amounts of 0.00018 ~ 0.00747% were detected in 7 thinners only. In addition, xylene was detected most frequently, and toluene and cellosolve materials were identified, similar to Paik's reports.

The content of benzene in all PDPs and thinner products showed a tendency to decrease with the year as shown in Fig. 2. However, until 2010, the maximum benzene content in all PDPs and thinner products exceeded 1% and 0.1% respectively. In terms of gasoline, benzene has been used to improve the octane value. However, with awareness of risks of benzene, the Korean criterion of benzene content in gasoline was gradually lowered from 6.0% in 1992 to 5% in 1996, 4% in 1998, 2% in 2000, 1.5% in 2002 and 0.7% in 2009 (ME, 2012; Sheen, 2001). Despite such regulation, analysis results showed that benzene contents in gasoline still exceed the 2002 criterion 1.5%, with some data reporting benzene contents as 6.0% in 2002 and 4.0% in 2007; and although the benzene content in gasoline criterion was reduced to 0.7% in 2009, 0.86% was reported in 2012. Tsai et al. (2017) reported that benzene content of commercial unleaded gasoline made in Taiwan, United States and Europe is 0.52% (v/v), 0.50-0.54% (v/v) and not available, respectively. Reducing the benzene content in gasoline is crucial for reduction of the benzene emissions during the combustion of auto vehicles. Yao et al. (2017) investigated organic air pollutant emissions from motorcycles by using various ethanol-gasoline blends. They reported that the content of benzene in commercial unleaded gasoline is 0.6%, and that as the mixing ratio of ethanol increases, the content of benzene decreases to 0.1%. When the mixing ratio of ethanol increases, the benzene emissions (mg km^{-1}) decreased from 8.9 mg km^{-1} with commercial gasoline to 4.2 mg km^{-1} with 30% (v/v) ethanol in gasoline.

Roh et al. (2000) reported that dry cleaning solvents used in Korean laundries were petroleum-based and contained more than 1% benzene. In 1990, about 53% of world demand for tetrachloroethylene was for dry cleaning used in USA, western Europe and Japan, and it was the cleaning fluid used by about 75% of all dry cleaners (Linak et al., 1992). However, more than 90% of the laundry solvents used in Korea until 2000 were petroleum-based solvents. Jeong et al. (2005) also investigated aromatic hydrocarbons contained in petroleum-based solvents used at 13 laundries in 2002, but only xylene was detected. Jeong et al. explained that domestic refiners are converting aromatics into naphthene compounds by adding a hydrogenation process to eliminate aromatic odors as much as possible.

Few studies have examined the benzene content in PDPs and personal exposure concentrations of handling workers. Only three of the eight articles investigating benzene content in PDPs reported airborne benzene exposure (Table 2). The benzene content in a product is one of the key factors that determine the benzene exposure level. However, exposure concentrations in air are affected by the conditions under which benzene containing products are handled, such as ventilation conditions, workplace temperatures, and length of time to handle the benzene-containing products (Kopstein, 2006). In a study by Song et al. (2000), gas station operators who handled gasoline with a benzene content of 2.1% to 5.9% were exposed to benzene in air at a concentration of 0.003 ppm to 0.2 ppm. On the other hand, Roh et al. (2001) reported that the geometric mean benzene exposure level of workers handling dry cleaning solvent contained 1.28%

of benzene was 1.43 ppm. Laundry workers workindoors, but because the work station workers work outdoors, there is a high probability that the benzene concentration in the air will be diluted.

To estimate benzene exposures of workers handling products containing trace amounts of benzene, a Similar Exposure Group (SEG) method can be used. Exposure estimation using the SEG has been verified in a simulation by Fedoruk et al (Fedoruk et al., 2003). Workers who handle products with known benzene contents and airborne exposure concentrations are used as a 'reference SEG'. Those who handle benzene-containing similar products under comparable working conditions are classified as a 'compared SEG'. The exposure level of the 'compared SEG' is estimated using a linear function in which the airborne exposure level increases in proportion to the benzene mole fraction according to the Raoult's law. In other words, as presented in Formula (4), the airborne benzene exposure concentration ($C_{ppm,\ SEG\text{-}C}$) of the 'compared SEG' is estimated by calculating the ratio of the benzene content (R_{Bz}) in the product used by the 'compared SEG' to that of the 'reference SEG' multiplied with the airborne exposure level ($C_{ppm,\ SEG\text{-}R}$) of the 'reference SEG'.

$$C_{ppm,\ SEG\text{-}C} = R_{Bz} \times C_{ppm,\ SEG\text{-}R} \text{ -------------------------- } (4)$$

In order to predict the benzene exposure well, there should be sufficient information on the operating conditions and work environment for the 'reference SEG'. Therefore, among the data on benzene contents in PDPs used in Korea and airborne exposure concentrations for handling workers, data that provide relatively enough information on work circumstances were used for SEG-based benzene exposure estimation, and the results are presented in Table 5.

Ro (1975) reported that the mean benzene content was 12.6% for 14 thinner products that were available at the time of the study and the airborne exposure concentration was 30 ppm for thinner-handling painting workers in a workplace with one LEV. Assuming the benzene content in thinner as 0.21%, workers' airborne exposure level under similar work conditions can reach

0.5 ppm, the current exposure criterion in Korea. Even at 0.1% of benzene in thinner, the exposure level can meet around the half level of exposure criterion of 0.5 ppm.

According to the epidemiological survey for a shipbuilding industry performed in 2002 by the KOSHA (OSHRI, 2013), the mean airborne exposure level of benzene was 0.92 ppm for spray painting workers, 0.06 ppm for brush painting workers and up to 6.5 ppm for painting workers in a confined block. Under similar work conditions, use of thinner with a benzene content of 0.1% and paint with a benzene content of 0.5% in a confined place may lead to a high-level exposure up to 65 ppm.

In an epidemiological survey of a lubricating oil production factory conducted in 2006 (OSHRI, 2013), the exposure level of workers engaged in raw material filling containing benzene of 1.1% was 0.37 ppm. Under similar work conditions, if the benzene content is assumed as 3%, the exposure level can reach the double level of domestic exposure criterion and if the benzene content is 0.3%, the exposure is expected to meet the USA NIOSH recommendation exposure level of 0.1 ppm.

The MSDS is a crucial means of providing information on a chemical and serves as a basis of a comprehensive chemical management system. It is recognized as a representative tool of information communication to prevent accidents and occupational diseases and satisfy workers' right to know by disclosing hazards and risks of a chemical and enabling its safe handling. However, as shown from Table 3, content information differed between product labels and MSDSs for 11 (34.4%) products and was consistent for only 5 (15.6%) products. Ten (31.3%) products had no content information in MSDSs, and MSDSs was not available for 6 (18.7%) products. In case of n-hexane, xylene and trichloroethylene, contents on product labels and MSDSs were inconsistent in all cases. Furthermore, no product had benzene listed as an ingredient.

As indicated by this study's findings, benzene is still included in PDPs not because it is used for a specific purpose, but it remains as an impurity. Consequently, products are being distributed and used with benzene unremoved. Kopstein (2006) explained several reasons for this. First, it is technically highly challenging to eliminate benzene, and second, it incurs high expenses to improve the efficiency of benzene impurity removal so that industrial-grade petrochemical products are used without eliminating benzene. Third, in separation of a mixture, it is not technically feasible yet to separate materials with similar boiling points. Such results suggest that if the presence of benzene is not specified in the MSDS and the label of a petrochemical product, workers who handle the product will engage in operations without recognizing that the product may contain benzene.

CONCLUSION

The benzene content in the PDPs is one of the key factors that determine the benzene exposure level. This study was conducted to assess benzene contents in PDPs through literature reviews reported in Korea, and also to estimate inhalable exposure to benzene of workers handling PDPs that contain trace amounts of benzene. Thinner had the highest benzene content of 56.7% in 1997, followed by 30.1% for printing agent in 2005, 8.96% for solvent used at maintenance and repair services of motor vehicles in 2005, and 6.0% for gasoline in 2002. The amount of benzene contained in the PDPs showed a declining trend by years, but workers treated with thinners containing less than 0.1% benzene were found to be exposed to concentrations above 1 ppm. Thirteen of the 32 reagents were also confirmed to contain benzene, while the products of trichlorethylene and ethylbenzene contained more than 0.1% benzene. However, no reagents had benzene information listed in MSDS or labeling as an ingredient. Even if the benzene content is below 0.1%, if there is a possibility of benzene exposure, it is warranted to specify presence of benzene in the MSDS to ensure protection of health of workers handling the PDPs. In terms of retrospective epidemiological survey for compensation, the information of benzene content in a PDPs handled by workers can be an important evidence to demonstrate the association between worker's disease and benzene exposure. Thus, this study results can be used as a basic information for estimation of benzene exposure to workers handling PDPs.

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REFERENCES

ACGIH (2001). Documentation of the threshold limit values (TLVs) and biological exposure indices (BEIs) - benzene.

Aitchison, J. and Brown, JAC. (1963). The lognormal distribution. Cambridge, UK: Cambridge University Press.

ATSDR (2007). Toxicological profile for benzene. U.S. Department of Health and Human Service. ASTDR. Atlanta (United States of America): Agency for Toxic Substances and Disease Registry. 243-244.

Fedoruk, M., Bronstein, R., and Kerger, B. (2003). Benzene exposure assessment for use of a mineral spirits-based degreaser. *Appl. Occup. Environ. Hyg.* 18 (10): 764-781.

IARC (2012). IARC monographs on the evaluation of carcinogenic risks to humans, chemical agents and related occupations volume 100F. A review of human carcinogens. Lyon (France): International Agency for Research on Cancer. 257-262.

Jeong, J.Y., Yi, G.Y., Lee, N., Lee, B.K., Kim, B.Y., and Kim, K.J. (2005). An evaluation of exposure to petroleum based dry cleaning solvent used in commercial dry cleaning shops. *J Korean Soc Occup Environ Hyg.* 15 (1): 19-26.

Kang, S.K., Lee, M.Y., Kim, T.K., Lee, J.O., and Ahn, Y.S. (2005). Occupational exposure to benzene in South Korea. *Chem Biol Interact.* 153-154: 65-74.

Kim, Y.Y., Yang, S.H., Lee, J.S., Lee, H.S., Jang, K.H., Jin, K.Y., Lee, Y.I., Joo, W.H., Paik, D.H., Kang, D.O., Moon, J.Y., Cho, Y.K., Park, D.U., Yoon, C.S., and Ha, K.C. (2006). Compositions and contents of thinner and reliability of MSDS sold in Busan and Gyeongnam province. *J Korean Soc Occup Environ Hyg.* 16 (4): 314-324.

KPIA (2012). 2012 Petrochemical products handbook. Korea Petrochemical Industry Association. Seoul.

Kopstein, M. (2006). Potential uses of petrochemical products can result in significant benzene exposure: MSDSs must list benzene as an ingredient. *J Occup Environ Hyg.* 3: 1-8.

Lee, J.Y., Kim, S.J., Lee, J.T., Moon, D.H., Lee, C.U., and Pae, K.T. (1990). Determination of organic solvent mixtures in shoes manufacturing industries. *Inje Medical Jaurnal.* 11 (4): 435-445.

Lee, K.S., Kwon, H.W., Han, I.S., Yu, I.S., and Lee, Y.M. (2003). A study on the reliability of Material Safety Data Sheets (MSDS) for paint thinner. *J Korean Soc Occup Environ Hyg.* 13 (3): 261-272.

Linak, E., Leder, A., and Yoshida, Y. (1992). C_2 chlorinated solvents. In: Chemical economics handbook, Menlo Park, CA, SRI International, pp. 632.3000–632.3001.

ME (2012). Clean air pollution act enforcement rules. Asterisk 33. Automotive fuel, additives or manufacturing of catalyst. Ordinance of the Ministry of Environment No.463, 1.

MOEL (2013). Standards on the classification, labeling and material safety data sheets of chemicals. Ministry of Labor Public Notice No. 2013-37, 8.

MOEL (2016). Exposure criteria for chemical and physical agents. Ministry of Employment and Labor Public Notice No. 2016-41.

OSHRI (2012). Casebook diagnosis of occupational diseases-2011. Occupational Safety and Health Research Institute. Korea.

OSHRI (2013). Epidemiological survey report for determination of an occupational disease case. Occupational Safety and Health Research Institute. Korea.

Paik, N.W., Yoon, C.S., Zoh, K.E., and Jung, H.M. (1998). A study on composition of thinners used in Korea. *J Korean Soc Occup Environ Hyg.* 8 (1): 105-114.

Park, D., Stewart, P.A., and Coble, J.B. (2009). A comprehensive review of the literature on exposure to metalworking fluids. *J. Occup. Environ. Hyg.* 6: 530-541.

Ro, D.S. (1975). A Study on threshold limit value of atmospheric environment for thinner-handling workers in Korea. *Journal of Korea University Medical School.* 12 (1): 183-193.

Roh, Y.M., Kwon, G.B., Park, S.H., and Jeong, J.Y. (2001). A survey on the management of chemical substances and airborne concentration in laundries exposed to organic solvents. *J Korean Soc Occup Environ Hyg.* 11 (1): 70-77.

Seixas, N.S., Robins, T.G., and Moulton, I.H. (1988). The use of geometric and arithmetic mean exposures in occupational epidemiology. *Am. J. Ind. Med.* 14: 465-477.

Sheen, D.H. (2001). Trends of qualities of gasoline and diesel fuels. *Fuel and Lubricant for Automotive Engines.* 23 (2): 13-19.

Shin, K.A. (1995). Qualitative analysis and quantification of VOCs in ambient air at gasoline service stations and roadsides. Graduate School Seoul City University Master's Thesis.

Song, S.H., Paik, N.W., and Ha, K.C. (2000). A study on exposure to volatile organic compounds at gas station in Korea. *J Korean Soc Occup Environ Hyg.* 10 (1): 58-73.

Tsai, J.H., Yao, Y.C., Huang, P.S., Chiang, H.L. (2017). Criteria pollutants and volatile organic compounds emitted from motorcycle exhaust under various regulation phases. *Aerosol Air Qual. Res.* 17: 1214–1223.

Williams, P., Panko, J., Unice, K., Brown, J., and Paustenbach, D. (2008). Occupational exposures associated with petroleum-derived products containing trace levels of benzene. *J Occup Environ Hyg.* 5: 565-574.

Yao, Y.C., Tsai, J.H., Wang, I.T. and Tsai, H.R. (2017). Investigating criteria and organic air pollutant emissions from motorcycles by using various ethanol-gasoline blends. *Aerosol Air Qual. Res.* 17: 167–175.

Table 1
Summary of the benzene content in domestic petrochemical products.

Products	<1980, %				1981 ~ 1999, %				≥2000, %				Total, %			
	N	WAM[b]	Min	Max	N	WAM	Min	Max	N	WAM	Min	Max	N	WAM	Min	Max
Adhesive					1	0.3	0.3	0.3	3	2.1	0.13	5.7	4	1.6	0.13	5.7
Cleaning products									2	0.8	0.17	1.5	2	0.8	0.17	1.5
Coating materials					2	0.4	0.01	0.7	21	0.16	0.00018	1.3	23	0.18	0.00018	1.3
Diluent									8	0.04	0.0026	0.3	8	0.04	0.0026	0.3
Gasoline					8	3.3	1	5.9	7	2.1	0.03	6	15	2.8	0.03	6
Hardener					2	1.9	1.8	2					2	1.9	1.8	2
Ink					2	0.4	0.2	0.5					2	0.4	0.21	0.5
Printing agent									2	15.2	0.25	30.1	2	15.2	0.25	30.1
Raw material									2	5.6	1.1	10	2	5.6	1.1	10
Solvent					9	0.3	0.016	1.0	3	3.6	0.5	9	12	1.14	0.016	9
Thinner	14	12.6	4	26.8	12	8.4	0.01	56.7	25	0.34	0.00018	2.1	51	5.7	0.00018	56.7
Others[a]					3	0.76	0.3	1.1	5	2.7	0.05	10.8	8	1.88	0.05	10.8
Total	14	12.6	4	26.8	40	3.2	0.01	56.7	78	1.53	0.00018	30.1	131	3.46	0.00018	56.7

[a] Accelerant, anti-rusting oil, ethylbenzene, fuel, release agent, toluene, waste
[b] Weighted Arithmetic Mean

Table 2

Summary of airborne exposure level of benzene to workers handling the benzene-containing petroleum-derived products.

Use	Product	Bulk content, %					Airborne 8hr time weighted average concentration of benzene, ppm							Reference
		Notation[a]	N	AM	MIN	MAX	Work	P/A[b]	N	GM(GSD)	AM	MIN	MAX	
Dilution or Washing	Thinner	V/V	14	12.6	4	26.8	Thinner handling at workplace A	P	8		30	18.5	51	Ro, 1975
							Thinner handling at workplace B	P	8		10	7.8	13.2	
Fuel	Gasoline	W/W	1	3.9			Gas station A	P	7	0.089		0.003	0.2	Song et al., 2000
								A	7	0.023		0.004	0.068	
		W/W	1	2.9			Gas station B	P	3	0.075		0.07	0.08	
								A	4	0.012		0.006	0.022	
		W/W	1	3.9			Gas station C	P	6	0.18		0.14	0.19	
								A	10	0.19		0.084	0.57	
		W/W	1	5.9			Gas station D	P	1	0.16				
								A	5	0.19		0.14	0.31	
		W/W	1	2.1			Gas station E	P	5	0.12		0.1	0.14	
								A	5	0.097		0.085	0.12	
		W/W	1	4.4			Gas station F	P	5	0.13		0.07	0.19	
								A	7	0.07		0.035	0.15	
		W/W	1	2.5			Gas station G	P	3	0.15		0.11	0.19	
								A	6	0.065		0.036	0.11	
Washing	Solvent	V/V	1	1.28			Laundry	P	17	1.43(2.63)				Roh et al., 2001
								A[c]	18	1.19(2.83)				
								A[d]	20	1.48(3.09)				
Tire manufacturing	Solvent	V/V	2	0.36	0.32	0.40	Extrude	P	14		0.55	0.31	0.84	OSHRI, 2013
	Release agent	V/V	1	0.3			Extrude	A	2		0.42	0.09	0.74	
							Mixing	A	1		2.16[e]			
Leather manufacturing	Coating materials	NR	1	0.7			Leather coating	P	7			0.02	0.05	OSHRI, 2013
	Solvent	NR	1	1										

	Catalyst	NR	1	0.9									
	Hardener	NR	1	2									
Parts of an automobile cluster development testing	Gasoline	V/V	1	4			Testing	P A	2 2	5.09 3.34	3.5 2.67	6.68 4	OSHRI, 2013
Adhesive	Adhesive	A/A	2	2.9	0.13	5.66	Adhesive	P	1	0.05			OSHRI, 2013
								A	2	0.06	0.05	0.06	
Painting	Thinner	A/A	1	0.01			Painting	P	5	1.53	0.01	6.55	OSHRI, 2013
	Coating materials		1	0.05									
Lubricant	Base oil	V/V	1	1.1			Filling	P	2	0.37	0.31	0.43	OSHRI, 2013

N, number of samples; GM, geometric mean; GSD, geometric standard deviation; AM, arithmetic mean; Min, minimum; Max, maximum

[a] A/A-area ratio, V/V-volumetric ratio, W/W-weight ratio, NR-not reported

[b] P-Personal, A-Area

[c] Air sampling around work table

[d] Air sampling around dry cleaner

[e] Short-term area sampling

Table 3

Experimental evidences on the evaluation of benzene contents in reagent chemicals.

ID	Reagent	Manufacturing			Purity, %		Benzene content, %		
		Nation	Company	Year	Labeling	MSDS	Labeling	MSDS	Bulk analysis
R-1	Cyclohexane	Korea	A	2013	99.5	100	NI[a]	NI	ND[b]
R-2	Cyclohexane	Korea	A	2013	99.8	100	NI	NI	ND
R-3	Cyclohexane	Japan	B	2004	98	NI[b]	NI	NI	ND
R-4	Cyclohexane	Japan	B	2013	99.5	NI	NI	NI	0.003
R-5	Cyclohexane	Japan	C	2013	>99.5	>99.5	NI	NI	ND
R-6	Cyclohexane	U.S.A.	D	2013	99.5	NI	NI	NI	ND
R-7	Ethylbenzene	Japan	E	2012	Minimum 98.0	Minimum 98.0	NI	NI	ND
R-8	Ethylbenzene	Japan	C	2013	> 99.0	> 99.0	NI	NI	0.142
R-9	Ethylbenzene	U.S.A.	D	2010	99.8	≤100	NI	NI	0.146
R-10	n-Heptane	Korea	A	2013	>98	100	NI	NI	ND
R-11	n-Heptane	Korea	A	2013	>99	100	NI	NI	ND
R-12	n-Heptane	Japan	B	2004	98	NI	NI	NI	ND
R-13	n-Heptane	Japan	B	2013	>99.0	NM[c]	NI	NM	ND
R-14	n-Heptane	Japan	C	2013	>99.0	>99.0	NI	NI	ND
R-15	n-Hexane	Korea	A	2013	>95.0	100	NI	NI	0.004
R-16	n-Hexane	Korea	A	2013	>96.0	100	NI	NI	ND
R-17	n-Hexane	Japan	B	2007	>96.0	NI	NI	NI	ND
R-18	n-Hexane	Japan	B	2013	>96.0	NM	NI	NM	ND
R-19	n-Hexane	U.S.A.	D	2013	95	NI	NI	NI	ND
R-20	Toluene	Korea	A	2012	>99.5	100	NI	NI	0.064
R-21	Toluene	Korea	A	2013	>99.7	100	NI	NI	0.063
R-22	Toluene	Japan	B	2004	>99.0	NI	NI	NI	0.014
R-23	Toluene	Japan	B	2004	>99.5	NI	NI	NI	ND
R-24	Toluene	Japan	B	2012	>99.7	NI	NI	NI	ND
R-25	Toluene	Japan	G	2004	99.7	NM	NI	NM	0.004
R-26	Toluene	Japan	C	2013	>99.5	>99.5	NI	NI	0.006
R-27	Trichloroethylene	Korea	A	2010	>98.5	98.5~100	NI	NI	ND
R-28	Trichloroethylene	Japan	B	2004	98	NM	NI	NM	0.166
R-29	Trichloroethylene	Japan	E	2013	>99.5	NM	NI	NM	ND
R-30	Xylene	Korea	A	2011	>80	100	NI	NI	0.009
R-31	Xylene	Japan	B	2004	>80	NI	NI	NI	0.006
R-32	Xylene	Japan	F	2004	>85	NM	NI	NM	0.006

MSDS, material safety data sheet

[a] No information, [b] Not detected, [c] No MSDS

Table 4
Comparison of benzene contents in thinners by the type of thinner.

Type of thinner	Benzene content, %			
	Ro (1975)	Paik et al. (1998)	Lee et al. (2003)	Kim et al. (2006)
Automobile painting thinner		ND[b]	0.00018~0.00747	
Coating thinner		56.7		ND
Degreasing thinner		23.3		
Electronic thinner		0.1		
Enamel thinner		0.3		0.3-1.2
Epoxy thinner		1.3		0.3-0.5
Lacquer thinner		0.6-2.8		
NC[a]	4.0-26.8			

[a] Not classified but toluene-based
[b] Not detected

Table 5

Estimation of benzene concentration by using a similar exposure group.

Reference similar exposure group					Compared similar exposure group	
Reference	Task	Product	Benzene content, % (1)	Airborne benzene concentration, ppm (2)	Benzene content, % (3)	Estimated airborne benzene concentration, ppm (4)[a]
Ro, 1975	Painting	Thinner	12.6	30	0.42	1
					0.21	0.5
					0.1	0.24
OSHRI, 2013	Painting	Thinner	0.01	0.92 (spraying)	0.1	9.2
		Coating materials	0.05		0.5	
				0.06 (brushing)		0.6
				6.5 (confined space)		65
OSHRI, 2013	Filling	Base oil	1.1	0.37	3.0	1
					1.5	0.5
					0.3	0.1

[a] (4) = (2)×(3)/(1)

Figure Captions

Fig. 1. Correlation between benzene and toluene content in 14 thinner products used in 1974 (Ro, 1975).

Fig. 2. Annual trends of the maximum benzene content in all petroleum-derived products (a) and thinner products (b) reported from 1975 to 2013 in Korea.

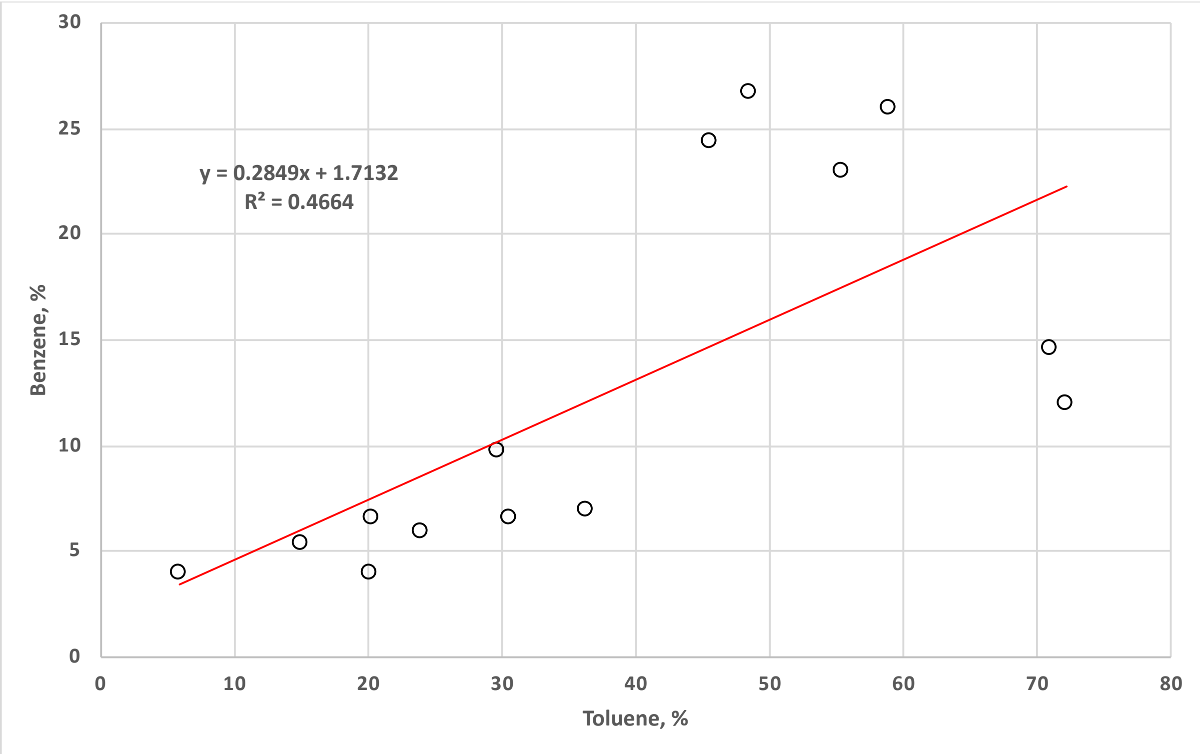
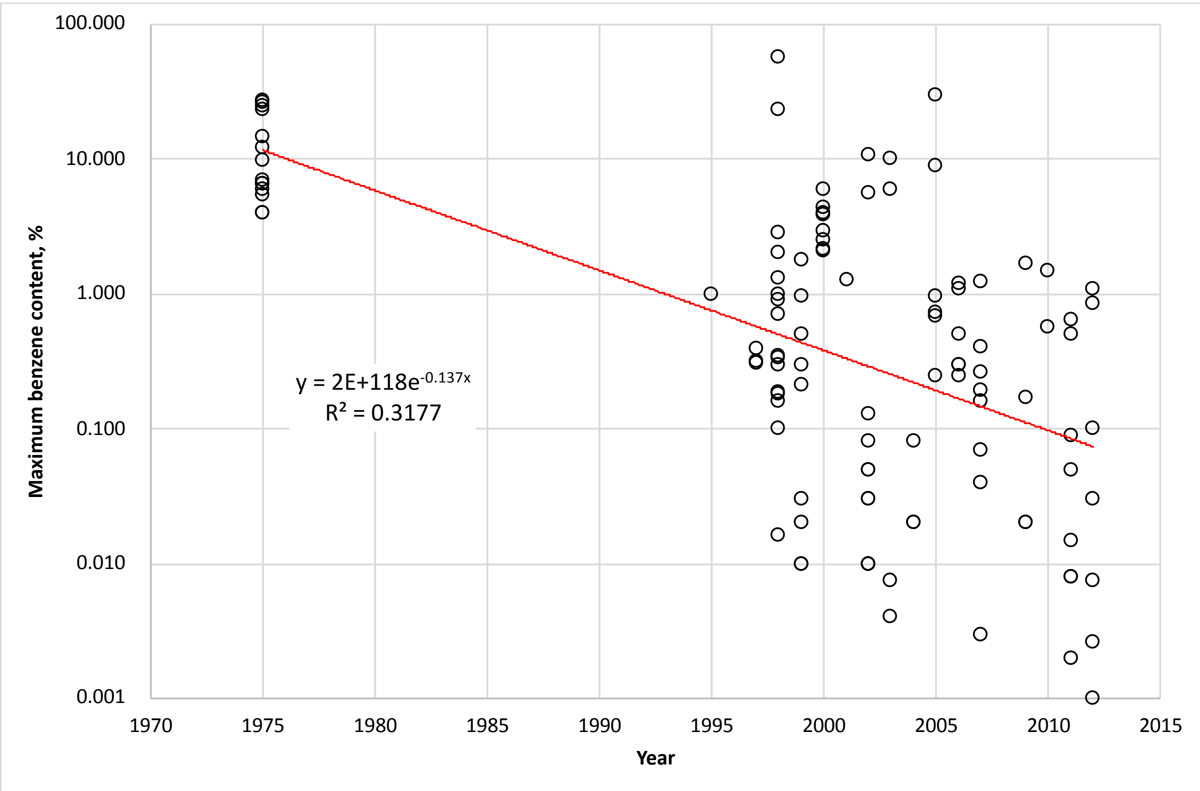
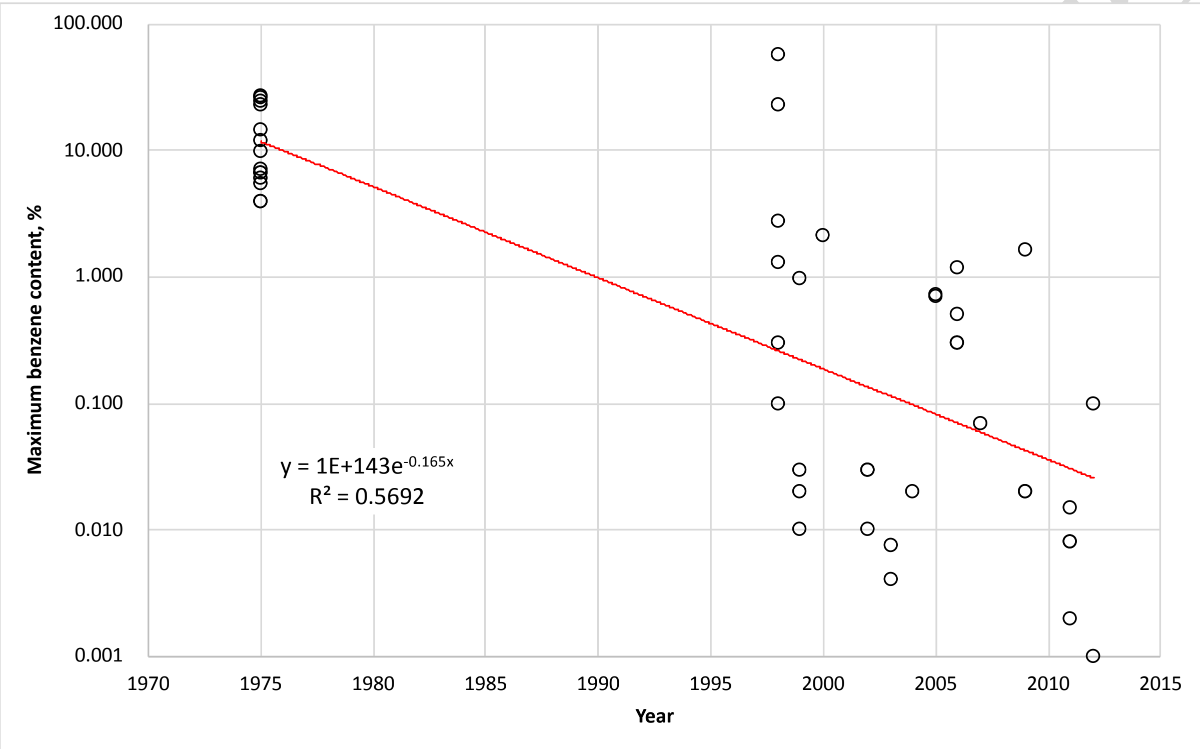

y = 0.2849x + 1.7132
R² = 0.4664
Benzene, %
Toluene, %
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
80

Fig 1.



100.000
10.000
1.000
0.100
0.010
0.001
Maximum benzene content, %
y = 2E+118e$^{-0.137x}$
R^2 = 0.3177
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Year

Fig 2. (a)



Maximum benzene content, %
100.000
10.000
1.000
0.100
0.010
0.001
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Year
y = 1E+143e-0.165x
R² = 0.5692

Fig 2. (b)