Greenpeace Research Laboratories Analytical Results 2015-08

Qualitative screening of surface wipe samples collected in the vicinity of the incident in Tianjin, China, 2015 for the presence of organic contaminants

November 2015

1. Introduction

Seven samples of surface wipes containing surface dusts, together with one unused field blank wipe and three identical unused wipes (direct from the supplying laboratory) were received at the Greenpeace Research Laboratories from Greenpeace East Asia (Beijing) on 16th September 2015. According to documentation supplied, the samples were collected between 28th August 2015 and 29th August 2015, at various locations in the vicinity of an explosion and fire in Tianjin, China, and at distances ranging from less than 1km to 3.6km from the blast, plus one control sample from a remote location located 60km from the site. Each of the samples collected surface dusts from an area of 30cm by 30cm.

The samples, control sample, laboratory blanks and field blanks were analysed qualitatively to investigate the presence of organic compounds in the dust captured on the surface of each sample wipe, correcting for any organic compounds arising from the material of the surface wipes themselves by using the field blank. Further details of the samples analysed are provided in Table 1.

2. Materials and methods

For each sample, a wipe was used to collect surface dust from an area of 30 cm by 30 cm. Following collection, the wipe was placed in a pre-cleaned 100ml glass bottle, which was immediately sealed. All wipe samples, control and blanks were prepared for analysis by extraction into a mixture of pentane and acetone using an accelerated solvent extraction (ASE) system, with both deuterated and brominated naphthalene as internal standards to control for extraction efficiency and extract volume. Extracts were analysed using an Agilent GC-MS system operated in both SCAN and SIM modes, and compounds identified using a combination of automated spectral matching against the Wiley 7N database and expert interpretation of spectra. In the case of PAHs, compound identities were further confirmed using retention times and specific ion fragment ratios in comparison to a mixed PAH standard run under identical conditions. More detailed descriptions of the sample preparation and analysis are provided in Appendix 1.

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GRL sample code	Sample type	Date collected	Distance from site (km)	location
CN15001-3	Lab blanks	n/a	n/a	Clean wipes provided by supplying laboratory
CN15004	Field blank	n/a	n/a	Unused wipe carried to field and returned
CN15005	Surface wipe	28.08.15	2.81 km	Student locker, school, first floor, near doorway
CN15006	Surface wipe	28.08.15	3.60 km	Window sill, Jiayuan Flat, 12th floor
CN15007	Surface wipe	29.08.15	0.79 km	Bathroom, tub, Harbour City, 13th floor, Building 16, west-facing.
CN15008	Surface wipe	29.08.15	2.30 km	Window glass, Yue Rong Xuan, 27th floor, Building 9
CN15009	Surface wipe	29.08.15	60 km	Cabinet in living room, Zhonghao Century Garden, 1st floor
CN15010	Surface wipe	28.08.15	2.80 km	Wood floor, gym stage (floor cleaned and waxed two days after the explosion)
CN15011	Surface wipe	29.08.15	0.78 km	Bathroom sink & wash table, Harbour City, 13th floor, Building 16, east-facing.

Table 1: details of samples received for analysis at the Greenpeace Research Laboratories

3. Results and Discussion

The organic compounds listed for each of the seven field samples (CN15005-11) in the results sheets in Appendices 2 and 3 are those compounds identified in the GC-MS screening analysis after correcting for any compounds that were also identified as components of the blanks (i.e. the unused surface wipes and field blank). The compounds listed can, therefore, be assumed to have been present in the dust or otherwise on the surfaces that were sampled with the wipes at the seven field locations.

These results are qualitative only; they report which substances were either reliably identified (with match qualities greater than 90%) or more tentatively identified (with match qualities between 51 and 90%), but do not give information on the concentrations of these substances in the samples. The PAHs listed in Appendix 3 were identified only in the more sensitive selective ion monitoring (SIM) mode.

The lists of compounds identified are dominated in most samples by long-chain hydrocarbons, which can arise from a variety of sources and origins, both internal and external. Other compounds that are common to many of the samples are:

- phthalate esters (especially dibutyl phthalate, diisobutylphthalate and bis(2-ethylhexyl) phthalate or DEHP), probably arising from their widespread use as plasticisers in PVC (vinyl) plastic materials or as solvents/carriers in other products.

- long-chain fatty acids and their derivatives (e.g. palmitic acid, methyl palmitate and palmate esters, and derivatives of oleic and stearic acid), possibly arising from their use in personal care products.

Other compounds identified in one or more samples were squalene (a natural component of human skin), musk xylene (a fragrance chemical still used in perfumes and personal care products in some parts of the world, though restricted or banned in others), caffeine (from coffee or energy drinks), nicotine (from cigarette smoke) and lanol (a natural component of wool). 4-nitrophenol was found in three of the samples (though neither of those located closest to the blast zone), possibly arising from its use to preserve and darken leather goods, though other sources cannot be ruled out.

A number of PAHs (polycyclic aromatic hydrocarbons) were also identified in SIM mode in 6 of the 7 field samples, including phenanthrene, fluoranthene and benzo[a]pyrene. Only small traces were detectable in sample CN15009 (06-01-03), collected 60km from the blast, but no PAHs could be detected at all in sample CN15011 (04-02-03), collected only 0.78km from the explosion site. PAHs commonly arise as products of incomplete combustion, including accidental explosions and fires, but can also be generated from a variety of other internal and external sources, including solid fuel or oil cooking and heating systems, traffic fumes and industrial sources. They are also present in some oils and other chemical preparations.

Overall, no clear relationship is observed in the qualitative data between the types or numbers of compounds identified, including PAHs, and the distance of the various sampling locations from the location of the explosion site. It is possible that this simply reflects (1) the small number of samples overall, (2) the variety of locations and surface types sampled, (3) differing levels of ventilation and cleanliness and therefore of the amounts and types of dust collected by the wipe sampling method and (4) the diversity of both internal and external sources possible for many of the chemicals identified.

No clear signature of residues which may have arisen from the explosion and subsequent fire is apparent from these results. A considerably larger and more extensive sampling programme in the vicinity of the explosion site and further afield would be necessary to investigate whether any such signature could be detected in the indoor dusts of households and public buildings as a result of the explosion. Given the potential significance of both indoor and outdoor dust as an accumulator of chemical contaminants and subsequently as a source of exposure, a more comprehensive study of this nature could play an important role in informing the overall assessment of impact from the accident and in guiding subsequent decontamination and clean-up measures in the vicinity.

For more information please contact: David Santillo or Melissa Wang

Disclaimer: Description of samples and sampling sites are purely according to information supplied with the samples by Greenpeace East Asia (Beijing).

Appendix 1: Details of methodologies

Preparation

Whole surface wipes were packed individually into small stainless steel accelerated solvent extraction cells, on top of a layer of activated and pre-cleaned Florisil to enable preliminary in-cell clean-up of the extract. 20 µg of deuterated naphthalene was added to the surface of the wipe as an Internal Standard (IS) and cell finally was topped up with the pre-cleaned diatomaceous earth sorbent (e.g., Hydromatrix). All wipe samples were extracted using a Dionex ASE 350 system with a 3:1 mixture of pentane/acetone. Obtained extracts were concentrated to a volume of 0.5ml under a stream of analytical-grade nitrogen using TurboVap system.

Each extract was further eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 1ml. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the qualitative organic compounds screening, samples were analysed using an Agilent 6890 GC with Restek Rxi-17Sil MS column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973N MSD operated in EI mode and interfaced with an Agilent Chemstation. The GC oven temperature program employed was as follows: an initial temperature of 40^0C, rising to 260^0C at 10^0C/min, then to 295^0C at 50^0C/min (held for 5 min), and finally to 325^0C at 50^0C/min (held for 4 min). The carrier gas was helium (Grade A), supplied at 1 ml/min, constant flow. Identification of compounds was carried out using the Agilent Chemstation software package utilizing the Wiley 7N library in combination with the expert judgment, as necessary, to avoid misidentifications.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory. Any background contaminants detected in blanks were subtracted from the chromatograms obtained for the samples before mass spectra were interpreted.

Appendix 2: organic compounds identified in surface wipe samples, following correction for compounds present in laboratory blanks (CN15001-3) and field blanks (CN15004).

CN15005: (02-01-03) Student locker, school, first floor, near doorway – 2.81km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
1-Octadecene	000112-88-9
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester	002082-79-3
Bis(2-ethylhexyl) phthalate	000117-81-7
Caffeine	000058-08-2
Cyclododecane	000294-62-2
Dibutyl phthalate	000084-74-2
Heptacosane	000593-49-7
Hexacosane	000630-01-3
Octacosane	000630-02-4
Phenol, 4-nitro-	000100-02-7
Tetracosane	000646-31-1
Tricosane	000638-67-5
Compounds tentatively identified (51-90% match):	
Diisobutyl phthalate	000084-69-5
Fluoranthene	000206-44-0

CN15006: (03-01-03) Window sill, Jiayuan Flat, 12th floor – 3.60km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
Cyclododecane	000294-62-2
Cyclohexadecane	000295-65-8
Dibutyl phthalate	000084-74-2
Dimethyl phthalate	000131-11-3
Heptadecane	000629-78-7
Hexadecanamide	000629-54-9
Hexadecane	000544-76-3
Hexadecanoic acid (Palmitic acid)	000057-10-3
Hexadecanoic acid, methyl ester (Methyl palmitate)	000112-39-0
Hexadecanoic acid, octadecyl ester (Stearyl palmitate)	002598-99-4
Nicotine	000054-11-5
Nonadecane	000629-92-5
Octacosane	000630-02-4
Pentacosane	000629-99-2
Pentadecane	000629-62-9
Tetracosane	000646-31-1
Tricosane	000638-67-5
Compounds tentatively identified (51-90% match):	
1-Docosene	001599-67-3
9-Octadecenamide, (Z)- (Oleic acid amide)	000301-02-0
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester	002082-79-3
Bis(2-ethylhexyl) phthalate	000117-81-7
Diisobutyl phthalate	000084-69-5
Formamide, N,N-dibutyl-	000761-65-9
Squalene	000111-01-3

CN15007: (04-01-03) Bathroom, tub, Harbour City, 13th floor, Building 16, west-facing – 0.79km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
1-Hexacosene	018835-33-1
1-Octadecene	000112-88-9
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester	002082-79-3
Benzothiazole	000095-16-9
Bis(2-ethylhexyl) phthalate	000117-81-7
Cyclotetracosane	000297-03-0
Dibutyl phthalate	000084-74-2
Dimethyl phthalate	000131-11-3
Docosane	000629-97-0
Dotriacontane	000544-85-4
Eicosane	000112-95-8
Erucylamide	000112-84-5
Heneicosane	000629-94-7
Hentriacontane	000630-04-6
Heptacosane	000593-49-7
Heptadecane	000629-78-7
Hexacosane	000630-01-3
Hexadecane	000544-76-3
Hexadecanoic acid, methyl ester (Methyl palmitate)	000112-39-0
Nonacosane	000630-03-5
Nonadecane	000629-92-5
Octacosane	000630-02-4
Pentacosane	000629-99-2
Pentadecane	000629-62-9
Tricosane	000638-67-5
Compounds tentatively identified (51-90% match):	
Squalene	000111-01-3

CN15008: (05-01-03) Window glass, Yue Rong Xuan, 27th floor, Building 9 – 2.30km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
1-Hexadecene	000629-73-2
9-Nonadecene	031035-07-1
Bis(2-ethylhexyl) phthalate	000117-81-7
Cyclododecane	000294-62-2
Dibutyl phthalate	000084-74-2
Docosane	000629-97-0
Eicosane	000112-95-8
Heneicosane	000629-94-7
Heptacosane	000593-49-7
Heptadecane	000629-78-7
Hexacosane	000630-01-3
Hexadecane	000544-76-3
Hexadecanoic acid, methyl ester (Methyl palmitate)	000112-39-0
Nonacosane	000630-03-5
Octacosane	000630-02-4
Octadecane	000593-45-3
Octadecanoic acid (Stearic acid)	000057-11-4
Phenol, 4-nitro-	000100-02-7
Squalene	000111-01-3
Tetracosane	000646-31-1
Tricosane	000638-67-5
5 other unidentified phthalate esters	n/a
Compounds tentatively identified (51-90% match):	
2-Pentanone, 3-methyl-	000565-61-7
Dimethyl phthalate	000131-11-3
Phenanthrene, 1-methyl-7-(1-methylethyl)-	000483-65-8

CN15009: (06-01-03) Cabinet in living room, Zhonghao Century Garden, 1st floor – 60km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
1-Docosene	001599-67-3
1-Hexacosene	018835-33-1
1-Nonadecene	018435-45-5
1-Octadecene	000112-88-9
9-Octadecenamide, (Z)- (Oleic acid amide)	000301-02-0
Bis(2-ethylhexyl) phthalate	000117-81-7
Cyclohexadecane, 1,2-diethyl-	
Decanal	000112-31-2
Dibutyl phthalate	000084-74-2
Docosane	000629-97-0
Dotriacontane	000544-85-4
Heneicosane	000629-94-7
Heptacosane	000593-49-7
Heptadecane	000629-78-7
Hexadecane	000544-76-3
Hexadecanoic acid, methyl ester (Methyl palmitate)	000112-39-0
Nonadecane	000629-92-5
Octadecane	000593-45-3
Palmitic acid, hexadecyl ester	000540-10-3
Palmitic acid, octadecyl ester	002598-99-4
Palmitic acid, tetradecyl ester	004536-26-9
Vitamin E acetate	000058-95-7
Unidentified phthalate	n/a
Compounds tentatively identified (51-90% match):	
Diisobutyl phthalate	000084-69-5
11,14-dimethoxy-12-hydroxy-abieta-8,11,13-triene	124183-25-1

CN15010: (02-02-03) Wood floor, gym stage (cleaned/waxed two days after explosion) – 2.8km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
1-Docosene	001599-67-3
1-Eicosanol	000629-96-9
1-Hexacosene	018835-33-1
1-Hexadecene	000629-73-2
1-Pentadecene	013360-61-7
9-Octadecenamide, (Z)- (Oleic acid amide)	000301-02-0
Bis(2-ethylhexyl) phthalate	000117-81-7
Caffeine	000058-08-2
Cholest-5-en-3-ol (3.beta.)- (Lanol)	000057-88-5
Dibutyl phthalate	000084-74-2
Erucylamide	000112-84-5
Heptacosane	000593-49-7
Heptadecane	000629-78-7
Hexacosane	000630-01-3
Hexadecane	000544-76-3
Hexadecanoic acid (Palmitic acid)	000057-10-3
Hexadecanoic acid, methyl ester (Methyl palmitate)	000112-39-0
Isopropyl Palmitate	000142-91-6
Musk xylene	000081-15-2
Nonacosane	000630-03-5
Nonadecane	000629-92-5
Octacosane	000630-02-4
Octadecanoic acid (Stearic acid)	000057-11-4
Pentacosane	000629-99-2
Pentadecane	000629-62-9
Pentadecane, 2,6,10,14-tetramethyl-	001921-70-6
Phenol, 4-nitro-	000100-02-7
Tetracosane	000646-31-1
Triacontane	000638-68-6
Tricosane	000638-67-5
Compounds tentatively identified (51-90% match):	
Benzothiazole	000095-16-9
Fluoranthene	000206-44-0
Hexadecanamide	000629-54-9

CN15011: (04-02-03) Bathroom sink, Harbour City, 13th floor, Building 16, east-facing – 0.78km from site	
Compound	**CAS No.**
Compounds reliably identified (>90% match):	
.gamma.-Sitosterol	000083-47-6
1-Nonadecene	018435-45-5
1-Octadecene	000112-88-9
1-Tricosene	018835-32-0
2,5-Heptadien-4-one (Phorone)	000504-20-1
Bis(2-ethylhexyl) phthalate	000117-81-7
Cholest-5-en-3-ol (3.beta.)- (Lanol)	000057-88-5
Compounds tentatively identified (51-90% match):	
9-Octadecenamide, (Z)- (Oleic acid amide)	000301-02-0
Octadecanal (Stearaldehyde)	000638-66-4
Tetradecanal	000124-25-4

Appendix 3: qualitative summary of PAHs identified in each of the samples (√ denotes compound identified, *t* indicates presence as small traces only)

GRL sample code	CN15005	CN15006	CN15007	CN15008	CN15009	CN15010	CN15011
Distance from site	**2.81km**	**3.60km**	**0.79km**	**2.30km**	**60km**	**2.80km**	**0.78km**
Acenaphthylene	√						
Fluorene	√						
Phenathrene	√	√	√	√		√	
Anthracene	√		√			√	
Fluoranthene		√	√	√	√*t*	√	
Pyrene		√	√	√	√*t*	√	
Benz[a]anthracene	√	√	√	√	√*t*	√	
Chrysene	√	√	√	√		√	
Benzo[b]fluoran-thene	√	√	√	√	√*t*	√	
Benzo[k]fluoran-thene	√	√	√	√	√*t*	√	
Benzo[a]pyrene	√		√	√		√	
Indeno[1,2,3-cd]pyrene	√	√	√	√		√	
Benzo[ghi]perylene	√	√	√	√		√	