

Survey of emissions of volatile organic chemicals from handheld toys for children above 3 years

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NILU report 12/2020 Norwegian Environment Agency M-1753 2020	ISBN: 978-82-425-3009-7 ISSN: 2464-3327	CLASSIFICATION: A – Unclassified (open report)
DATE 13.07.2020	SIGNATURE OF RESPONSIBLE PERSON Aasmund F. Vik (sign.)	NUMBER OF PAGES 12
TITLE Survey of emissions of volatile organic chemicals from handheld toys for children above 3 years		PROJECT LEADER Pernilla Bohlin-Nizzetto
		NILU PROJECT NO. O-119128
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REPORT PREPARED FOR Norwegian Environment Agency		CONTRACT REF. 19087602
ABSTRACT <p>NILU has, on behalf of the Norwegian Environment Agency, performed a screening study to identify volatile organic chemicals (VOCs) emitted from handheld toys for children. The goal was to identify individual VOCs emitted from toys at room temperature and to evaluate what impact the toys may have on the composition and concentrations of VOCs in indoor air. 12-30 individual VOCs were identified in each toy and 65-143 individual VOCs were detected with a concentration higher than 1 µg/m³. VOCs emitted at high concentrations and/or with hazardous properties were cyclohexanone, aromatic VOCs (xylenes, toluene, ethylbenzene), cyclic siloxanes and 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (TXIB). A regulated hydrochlorofluorocarbon (HCFC-141 b) was also detected from 5 toys. The toys with high concentrations of cyclohexanone and cyclic siloxanes affected the composition and concentrations of VOCs in indoor air.</p>		
NORWEGIAN TITLE Kartlegging av avdampning av kjemikalier fra håndholdte leketøy for barn over 3 år		
KEYWORDS VOC – volatile organic compounds Indoor environment Environmental chemistry		
ABSTRACT (in Norwegian) <p>NILU har på oppdrag av Miljødirektoratet utført en kartleggingsstudie av avdampning av flyktige organiske forbindelser (VOC) fra håndholdte leketøy for barn. Formålet med studien var å identifisere enkel-VOCer som dampes av fra leker i romtemperatur og å vurdere påvirkning på sammensetning og nivåer av VOCer i inneluft. 12-30 enkel-VOCer ble identifisert fra hver leke og 65-143 enkel-VOCer med konsentrasjoner høyere enn 1 µg/m³ ble detektert. VOCer som ble målt i høye konsentrasjoner og/eller med helse- og miljøfarlige egenskaper var sykloheksanon, aromatiske VOCer (xylener, toluen, etylbenzen), sykliske siloksaner and 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (TXIB). I tillegg ble en regulert hydroklorfluorkarbon (HKFK- 141 b) detektert fra fem leker. Lekene med høyest konsentrasjoner av sykloheksanon og sykliske siloksaner påvirket sammensetningen og konsentrasjonene av VOCer i inneluft.</p>		
PUBLICATION TYPE: Digital document (pdf)	COVER PICTURE: Source: NILU	

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Summary

NILU has, on behalf of the Norwegian Environment Agency, performed a screening study to identify volatile organic chemicals (VOCs) emitted from handheld toys for children. The main goal was to identify individual VOCs emitted from toys at room temperature and to prioritize the identified VOCs based on hazardous properties. The second goal of the study was to evaluate what impact the toys may have on the composition and concentrations of VOCs in indoor air.

The study was split in two parts. In part 1, the VOCs emitted from individual toys were identified and quantified using inert and air-tight plastic bags together with passive air samplers based on Tenax TA adsorbent. In part 2, the contribution of highly emitting toys to indoor VOC composition and concentrations in air were measured by placing selected toys in a typical child room and measuring the VOC concentrations with Tenax TA air samplers at three locations in the apartment. Thermal desorption (TD) and gas chromatography coupled to mass spectrometer (GC-MS) in combination with commercial and in-house database was used for identification and quantification of the VOC content in all air samples.

The results showed that 12-30 individual VOCs were identified in each toy and 65-143 individual VOCs were detected with a concentration higher than $1 \mu\text{g}/\text{m}^3$ and included in total VOC concentration. The TVOC for the identified VOCs ranged from 200-265 000 $\mu\text{g}/\text{m}^3$ and between 240 and 304 000 $\mu\text{g}/\text{m}^3$ (0.24–304 mg/m^3) when including all VOCs present at concentrations higher than $1 \mu\text{g}/\text{m}^3$. VOCs at high concentrations and/or hazardous properties were cyclohexanone, aromatic VOCs (xylenes, toluene, ethylbenzene), cyclic siloxanes and 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (TXIB). Also a regulated hydrochlorofluorocarbon (HCFC-141 b) was emitted from 5 out of 45 toys. The results of the measurements in the apartment with the high-emitting toys show that toys with high concentrations of cyclohexanone and cyclic siloxanes affects the composition and concentrations of VOCs in indoor air. The toys with high concentrations of TXIB and aromatic VOCs did in this study not affect the indoor air.

Survey of emissions of volatile organic chemicals from handheld toys for children above 3 years

1 Introduction

NILU – Norwegian Institute for Air Research on behalf of the Norwegian Environment Agency, has performed a screening study to identify and quantify volatile organic chemicals (VOCs) emitted from handheld toys for children above 3 years. The main goal of the study was to identify and quantify individual VOCs emitted from individual toys at room temperature, and to prioritize the identified VOCs based on hazardous properties. The second goal was to evaluate what impact the highly emitting toys may have on the composition and concentrations of VOCs in indoor air.



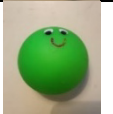




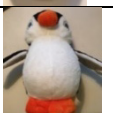

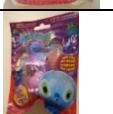



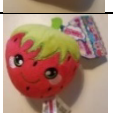
In recent years, studies have shown that the emissions of some VOCs from toys are high and may pose a significant risk to children's health.¹ In order to minimize children's exposure to undesirable organic chemicals, it is important to identify which VOCs that are emitted from toys and further can lead to adverse exposure through inhalation.

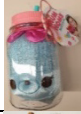














2 Samples



All the toys in the study (n=45) were selected and purchased by the Norwegian Environment Agency. A complete list of all samples is given in Table 1.

Table 1: Handheld toys for children selected and purchased for this study with information on those selected for part 2.

Sample nr.	Name/Type		Part 2
1	My Little Pony		Group A)
2	Skippy Unicorn		Group C)
3	Funville, Sparkle girlz unicorns		
4	Gloopers, Dracus Flammucus		
5	Paw Patrol, Squishy		
6	Sweet Pups		
7	Foam alive		

Sample nr.	Name/Type		Part 2
8	Mini cupcake surprise		
9	Exogini		
10	Bubleeze, unicorn		
11	Grønn klemboll		
12	Hair dooz		Group C)
13	Designerz, Squishy		
14	Pinapple, Squishy		Group C)
15	Cutie Tooties Surprise, Grønn		Group D)
16	Squishy for love, Penguin		
17	Cutie Tooties Surprise, Orange		Group D)
18	Odditeez Swellihedz		Group B)
19	Rainbocorns		Group D)
20	Odditeez Splatzeez		Group B)
21	Squeezamals, Cake		
22	Squeezamals, Strawberry		

Sample nr.	Name/Type		Part 2
23	Num Noms, Surprise Jar		
24	Squishy fur love, Rabbit		
25	Cupcake Surprise		
26	Puffimals		
27	Puffer poodle		
28	Shopkins Shoppies, Jessica		
29	Dino world, Hand puppet		
30	Sticky Poop, Stretch ball		
31	Avengers bubblez		
32	Bog-eyed Bugglies		Group B)
33	Puffer, Worm		
34	Werewolf, mask		
35	Devil, mask		
36	Velociraptor, mask		
37	Super Hydro, Slime		

Sample nr.	Name/Type		Part 2
38	Num Noms, Shimmer Sweets		
39	Doll		Group A)
40	Fruity Slime, Yellow		
41	Fruity Slime, Orange		
42	Clever Reptile		Group C)
43	Puffer ball, Pink		
44	Puffer ball, Yellow		
45	Safari animals		

3 Emission test

3.1 Part 1 Measurement of VOCs emitted from toys

In the first part of the study, the emission of VOCs from the selected toys was measured by placing the toys, individually, in inert and airtight plastic ziplock bags together with a passive air sampler. The toys were taken out of their packages and directly placed in the ziplock bags (Figure 1). Some of the toys were also further opened and assembled to recall actual usage. The passive air samplers used in this study were based on Tenax TA adsorption tubes. Before exposure, all Tenax TA tubes were re-conditioned and pre-cleaned by thermal desorption and immediately sealed with Swagelock end caps to minimize risk of contamination. One Tenax TA tube was placed inside the plastic bag together with the individual toy (Figure 1), making sure they were not in direct contact. The bag was filled with zero air, sealed and the Tenax TA tube was exposed for 24 hours at room temperature. The adsorption tubes were then directly transferred to chemical analysis.



Figure 1 Part 1 – Measurements of VOC emissions in an inert atmosphere using Tenax TA passive air samplers.

3.2 Part 2 Measurements of VOCs emitted from highly emitting toys to indoor air

In the second part of the study, the emission of VOCs from a selection of toys to indoor air was measured. The selection of toys was based on the results from part 1 and resulted in 12 toys in part 2. The 12 toys were grouped in four groups based on the highest emitted VOCs (Table 1):

- A) TXIB – toy nr. 1 and 39;
- B) Aromatic VOCs – toy nr. 18, 20 and 32;
- C) Cyclohexanone – toy nr. 2, 12, 14 and 42;
- D) Siloxanes – toy nr. 15, 17 and 19.

The emissions from each group of toys was performed in a furnished apartment (40 m²) without any current residents. There were no personal care products, cleaning products or clothes in the apartment. The toys within one group were placed on a bed in a small bedroom (6 m²). Sampling of VOCs was done at three locations in the apartment. One air sampler was placed next to the toys in the bed (in order to resemble the breathing zone of a child), the second air sampler was placed in the other end of the bedroom and the third in the living room at the other side of the apartment. All samples were collected using Tenax TA adsorption tubes that were connected to a critical orifice connected to evacuated stainless steel canisters (6 L). This set-up allowed for a constant air flow over a 10 hr sampling period and results in a total sample volume of 6 L (10 mL/min). The measurements gave a good average concentration during 10 hr of exposure. One group of toys was placed in the bedroom at a time, removed after sampling and the apartment was aired for 24 hrs before the next group was introduced. The Tenax TA adsorption tubes were directly transferred for chemical analysis.

4 Chemical analysis

The Tenax TA tubes were analyzed for VOCs using automated thermal desorption (TD) and gas chromatography coupled to mass spectrometer (GC-MS). Shortly, the TD operated at one stage desorbing-mode in which the Tenax TA tubes were desorbed at 250°C for 10 min and trapped on a cryo focussing trap at -30°C, injected to the GC-MS by rapid heating of the cold trap .

The obtained chromatograms were automatically and manually checked for identification of VOCs using commercially available and in-house libraries.

The concentrations of the identified individual VOCs are expressed in "Toluene Equivalents" and ranged hereafter. In addition, also the so-called "total VOC" (TVOC) expressed in "Toluene Equivalents" was obtained for the individual samples. One TVOC was obtained for the identified VOCs and one TVOC was obtained for the total number of compounds with a concentration above 1.0 µg/m³. The identified VOCs were ranked after concentrations .

5 Results

5.1 Part 1

The identified compounds (name and CAS-number) and the quantified concentrations in the individual toys (n=45) are presented in Annex 1 (Excel file).

5.2 Part 2

Detailed results from the individual measurements (n=12) are presented in Annex 2 (Excel file). A summary is also given in Table 2.

Group A) TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)

TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate) was detected at highest concentration from toy 1 (1 725 µg/m³) and toy 39 (1 026 µg/m³) in part 1 of this study. The concentration of TXIB in the air closest to the toys, "breathing zone", was 2 µg/m³ while it was about 10 times lower at the other end of the bedroom and in the other part of the apartment (0.4 µg/m³). At all three locations, TXIB was measured at lower concentrations than typical indoor VOCs from wood materials (α-pinene, acetic acid and 3-carene). The TVOC of identified VOCs were 17-31 µg/m³ during this measurement.

Group B) Aromatic VOCs

The three toys included in this group (18, 20 and 32) emitted high concentrations of xylenes (2 500-6 000 µg/m³) and other volatile aromatic compounds in part 1. Despite the high concentrations in part 1, all of the aromatic VOCs were observed at low concentrations or were not detected at the three locations in the apartment (part 2). The detected concentrations were below the concentrations of typical indoor VOCs from wood materials (α-pinene, acetic acid and 3-carene). The TVOC of identified VOCs were 2-15 µg/m³ during this measurement.

Group C) Cyclohexanone

Cyclohexanone was detected at high concentrations from toy 2, 12, 14 and 42 (2 000-12 000 µg/m³) in part 1. It was also the dominant VOC in air at all three locations in part 2 with concentrations of 100 µg/m³ closest to the toys and 35 µg/m³ at the other end of the room and in the living room. None of the typical indoor VOCs measured at highest concentrations in group a and b were detected when adding the toys in group c in the apartment. The concentrations of cyclohexanone measured here are higher than the "normal" concentrations in air in Norwegian indoor environments. These toys also resulted in detection of several other VOCs at elevated concentrations; 5-26 µg/m³ at the breathing zone and 2-10 µg/m³ at the other two locations. As a result higher concentrations of TVOC (120-370 µg/m³) were measured when group c toys were added in the apartment.

Group D) Siloxanes

The toys selected for this group (15, 17 and 19) resulted in air concentrations of 2 500-44 000 $\mu\text{g}/\text{m}^3$ of the oligomer D4 (octamethylcyclotetrasiloxane), in part 1. D4 was also the dominant VOC measured at all locations in part 2 with 270 $\mu\text{g}/\text{m}^3$ closest to the toys, 73 $\mu\text{g}/\text{m}^3$ in the other end of the bedroom and 37 $\mu\text{g}/\text{m}^3$ in the living room. The other siloxane oligomers D5 (decamethylcyclopentasiloxane), D3 (hexamethylcyclotrisiloxane), and D6 (dodecamethylcyclohexasiloxane) were lower than D4 but still measured at elevated concentrations at all three locations in the apartment. This resulted in elevated concentrations of TVOCs in the indoor air (94-680 $\mu\text{g}/\text{m}^3$). Also the toys in this group resulted in detection of several other VOCs at elevated concentrations, above the typical indoor VOCs, in the apartment (e.g. xylenes, cyclohexanone etc).

Table 2 Summary of results in part 2 of the study. Presented are the five VOCs detected at highest concentrations together with the TVOC at each location ($\mu\text{g}/\text{m}^3$) when adding the toys of each group.

	Group A (TXIB): $\mu\text{g}/\text{m}^3$	Group B (Aromatic VOCs): $\mu\text{g}/\text{m}^3$	Group C (Cyclohexanone): $\mu\text{g}/\text{m}^3$	Group D (Siloxanes): $\mu\text{g}/\text{m}^3$
Breathing zone (bed)	α -pinene: 4.2 Nonanal: 3.0 TXIB: 2.0 3-carene: 1.5 Ethylbenzene: 1.4 TVOC: 17	Acetic acid: 5.6 α -pinene: 1.6 Nonanal: 1.2 Hexanal: 0.9 Benzaldehyde: 0.8 TVOC: 12	Cyclohexanone: 98 Naphthalene, decahydro-2,3-dimethyl-: 26 Cis,trans-1,6-Dimethyl-spiro[4.5]decane: 18 Trans-Decalin, 2-methyl: 18 Tridecane: 17 TVOC: 370	Cyclotetrasiloxane, octamethyl-: 272 Cyclopentasiloxane, decamethyl-: 71 Cyclotrisiloxane, hexamethyl-: 68 Cyclohexane, 1,1-dimethyl-: 26 Cyclohexanone: 25 TVOC: 680
Bedroom	Acetic acid: 8.0 α -pinene: 4.2 Nonanal: 3.0 Benzaldehyde: 1.5 3-carene: 1.5 TVOC: 25	Acetic acid: 1.6 Hexamethyl cyclo-trisiloxane (D3): 0.3 α -pinene: 0.2 TXIB: 0.2 TVOC: 2.3	Cyclohexanone: 35 Naphthalene, decahydro-2,3-dimethyl-: 9.7 Naphthalene, decahydro-2,6-dimethyl-: 6.5 1-butanol: 6.4 Naphthalene, decahydro-2-methyl-: 6.1 TVOC: 120	Cyclotetrasiloxane, octamethyl-: 73 Cyclopentasiloxane, decamethyl-: 15 Cyclotrisiloxane, hexamethyl-: 14 Cyclohexanone: 6.3 Cyclohexane, 1,1-dimethyl-: 4.5 TVOC: 150
Living room	Acetic acid: 6.4 α -pinene: 5.2 Nonanal: 4.4 Decanal: 2.7 Octanal: 2.0 TVOC: 31	Acetic acid: 4.9 Nonanal: 2.7 α -pinene: 1.5 Benzaldehyde: 1.3 Decanal: 1.0 TVOC: 15	Cyclohexanone: 35 Naphthalene, decahydro-2,6-dimethyl-: 11 1-butanol: 7.6 Cis,trans-1,6-Dimethylspiro[4.5]decane: 6.7 Trans-Decalin, 2-methyl: 6.5 TVOC: 136	Cyclotetrasiloxane, octamethyl-: 37 Cyclopentasiloxane, decamethyl-: 8.8 Pentane: 6.8 Cyclotrisiloxane, hexamethyl-: 5.0 Cyclohexanone: 4.3 TVOC: 94

6 Discussion

Emission of high concentrations and a wide-range of VOC compounds from handheld toys were identified and quantified by the passive Tenax TA air samplers. The results showed that 12-30 individual VOCs were identified in each sample and 65-143 individual VOCs were detected with a concentration higher than $1 \mu\text{g}/\text{m}^3$. The TVOC concentrations for the identified VOCs in the individual toys ranged from 200-265 000 $\mu\text{g}/\text{m}^3$ (0.20–265 mg/m^3) and between 240 and 304 000 $\mu\text{g}/\text{m}^3$ (0.24–304 mg/m^3) when including all VOCs present at concentrations higher than $1 \mu\text{g}/\text{m}^3$. The highest concentration of TVOC was measured in toy 17, Cutie Tooties Surprise Orange, (304 mg/m^3) followed by toy 2, Skippy Unicorn, (142 mg/m^3). Of the individual VOCs identified in the toys, the highest concentrations were measured for aromatic VOCs (xylenes, ethylbenzene etc.), cyclohexanone, cyclic siloxanes, TXIB as well for some alcohols.

The results from part 2 showed that the emission of cyclohexanone and cyclic siloxanes from handheld toys affect the concentrations in indoor air and can thereby pose a risk for children. Cyclohexanone is not a typical indoor VOC and the presence of cyclohexanone in the measurements of part 2 show that the toys with high concentrations of cyclohexanone (especially the one with the highest concentrations) affect indoor air concentrations. The same was observed for the cyclic siloxanes that also resulted in elevated indoor concentrations.

In contrast, the high emissions of TXIB and aromatic VOCs from handheld toys did not influence the VOC concentrations in indoor air, in this study, although these VOCs were quantifiable at most locations. One reason for this may be that the aromatic VOCs already had evaporated from the toys during part 1 and the storage between November and February. This was confirmed by less aromatic smells of the toys when placed in the room in part 2 than in part 1. TXIB is less volatile than most of the other identified VOCs. TXIB will also deposit on most surfaces and particles in the indoor environment and thereby being less measurable in the gas-phase. Once emitted into indoor air, TXIB will always re-evaporate from surfaces to a certain extent and therefore persist longer in the indoor environment than other more volatile VOCs. It is recommended to re-do measurements with new toys before conclusions for TXIB and aromatic VOCs are taken.

In addition to the hazardous substances also one regulated hydrochlorofluorocarbon (HCFC) was emitted from 5 out of 45 toys. The HCFC-141 b (Cas. nr. 1717-00-6); 1,1-Dichloro-1-fluoroethane is regulated within the frame of the Montreal Protocol and known for its - amongst HCFCs - quite high Ozone Depleting Potential. HCFC 141b was also detected and identified in 5 out of 8 squishy toys in a report from the Danish Environmental Agency¹. Those findings were, however, without any further comments within the report. The measurement and sampling techniques – used within this screening project - are not fully quantitative for HCFCs. Despite that, we could detect and identify HCFC 141b in 5 different toys within the first 30 compounds (ranked after their emission strength). Toy nr 5 had the highest concentrations of HCFC 141b with 834 $\mu\text{g}/\text{m}^3$ while toy nr 10, nr 11, nr 13 and nr 14 had concentrations between 12 and 29 $\mu\text{g}/\text{m}^3$. All of those toys are made in China. In order to confirm the findings of HCFC in toys and quantify with a more suitable method - identical toys were analyzed in a follow-up project in May 2020.

7 References

1. Danish Environmental Protection Agency (2018) Undersøgelse og risikioverurdering af parfume og andre organiske stoffer i squishy legetøj.

NILU – Norwegian Institute for Air Research

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NILU's values: Integrity - Competence - Benefit to society

NILU's vision: Research for a clean atmosphere

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ISBN: 978-82-425-3009-7
ISSN: 2464-3327