

Sample Preparation, Extraction and Analysis of Imported Children's Toys for Bisphenol A and Phthalates



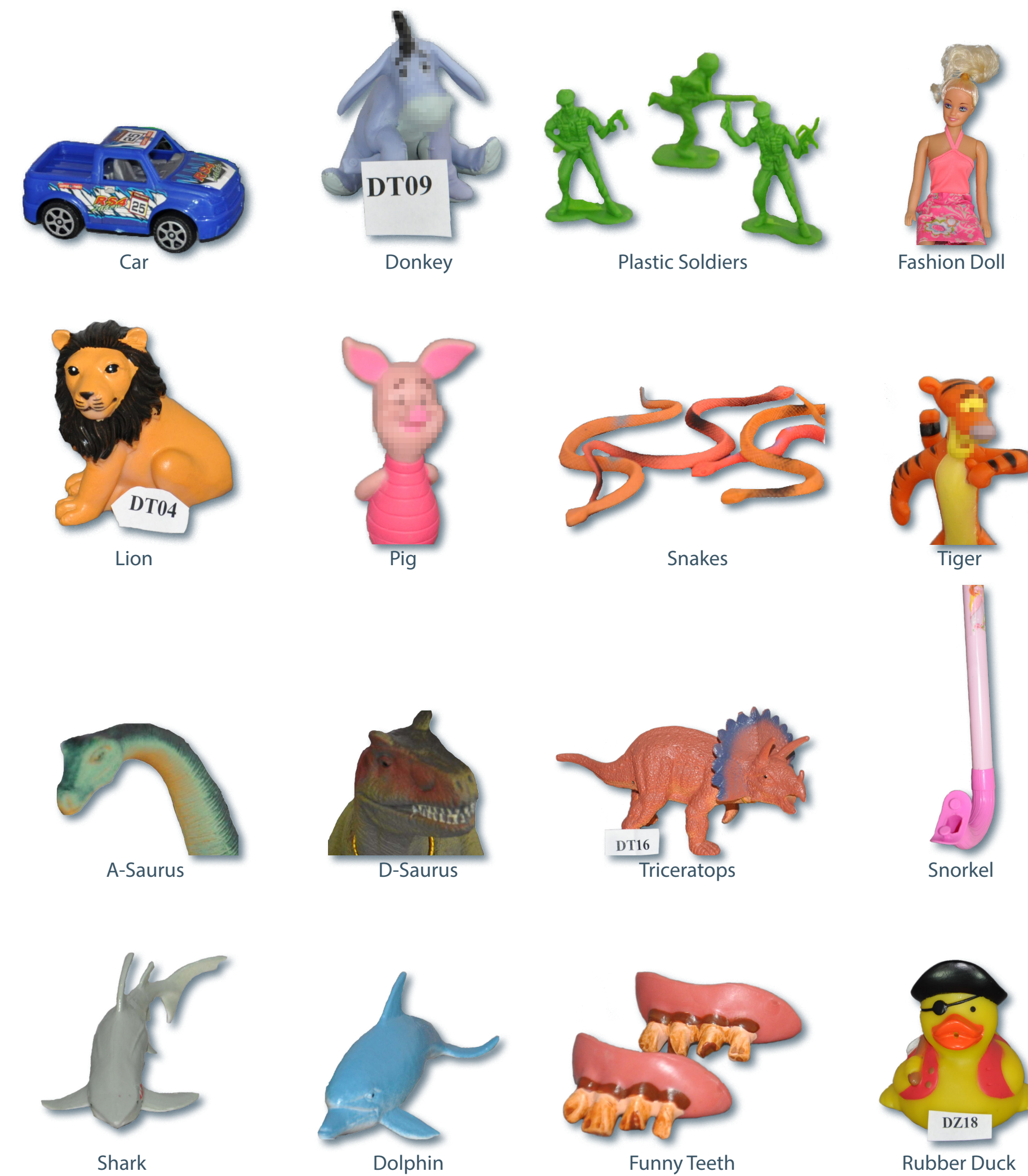
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Abstract

The US has started to limit levels of some phthalates for use in children's products including DEHP, DBP, BBP, DINP, DIDP & DIOP. The Consumer Product Safety Commission (CPSC) has published testing methods for these regulated phthalates. The regulation of Bisphenol A (BPA) remains under debate. This study examined the levels of phthalates and BPA in 26 children's toys purchased from local discount or 'dollar'-type stores. The toys were all reported as being made in China.

Microwave extraction methods were created and optimized against SPEX CertiPrep certified solid reference materials to compare levels of phthalates and BPA found in the toys. Samples were examined using GC-MS. High levels of phthalates and BPA were detected in the majority of the PVC toys. In many samples the concentration of phthalates far exceeded the limits set by the CPSC.

Toy Samples

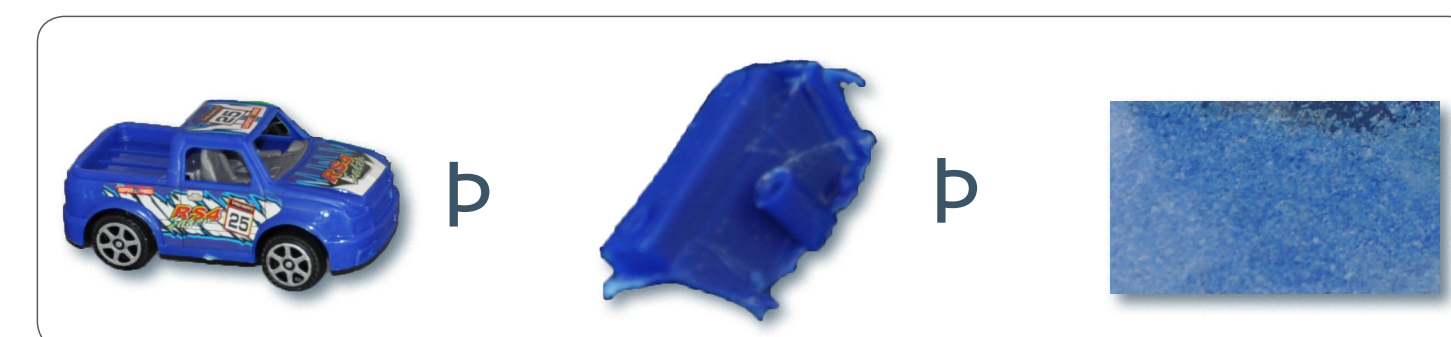


Type of Material	# Samples
LDPE	22
PVC	18
PC	7
HDPE	6
PP	2
Cloth Textile	1
Silicone	1

Methods and Materials

Sample Preparation

- 26 toys were separated by material type and coloration
- Composite toys were subdivided into constituent parts and materials
- 26 toys became 57 samples
- Paint was not removed from painted surfaces, but surface stickers were removed prior to further processing



- Toys cut up into 5 mm pieces and ground to a fine power using SPEX SamplePrep 6970 Freezer/Mill® with the Multi-Vial Adapter and 6571 Vials
- Two to three grams of toy material were ground
- Cryogenic program:
 - Twenty minutes of precool followed by five cycles of grinding at 2 minutes per cycle
 - Each cycle followed by two minutes of cooling
 - Impact rate was 16 impacts per second
- The plastic toys were identified with density and chemical testing



Sample Extraction

Two different extraction methods were employed against a corresponding plastic standard to determine extraction efficiency. The first method was a dissolution/precipitation method outlined in the CPSC method: CPSC-CH-C1001-09.03.

Precipitation Extraction Method:

- 0.05 g of a PVC sample was dissolved into 5 mL THF and precipitated with 10 mL Hexane. PVC and HDPE toy samples were extracted using this method with a matching PE and PVC certified reference material containing phthalates (CRM-PE001).
- Recovery data showed that the extraction efficiency for this method for the PE matrix was 50%. The extraction efficiency for the PVC matrix using this method was 83-94%. The PVC matrix had higher efficiency than the PE matrix but the RSD for subsequent GCMS ranged from 35 – 60% showing a possible contamination issue of the GCMS system by polymer still in solution.

Microwave Extraction Method:

Microwave extraction methods for phthalate extraction for Polyethylene and Polyvinyl Chloride were developed to maximize the recovery of phthalates from each type of plastic matrix. 0.2 g of sample were extracted using a CEM Mars Microwave system with Xpress Vessels.

Polyethylene Extraction Method:

- 10 mL Cyclohexane: Acetone (30:70)
- Ramp to Temp
- 10 min. to 140 °C
- Hold 10 minutes
- Stirring: On

Polyvinyl Chloride Extraction Method:

- 10 mL Cyclohexane: IPA (50:50)
- Ramp to Temp
- 10 min. to 130 °C
- Hold 10 minutes
- Stirring: On

Comparisons of the CPSC precipitation method and the microwave extraction method showed increased recovery and reduced %RSD results. The recovery of PVC increased from 85-94% to >95% by using the optimized microwave extraction method. The %RSD for the microwave method was less than 2.5% for all the targeted phthalates.

Table 2. Comparison of RSD between CPSC and Microwave methods

Compound	Optimized Microwave Method for PVC (%RSD)	CPSC Wet Method for PC (%RSD)
Di-n-butyl phthalate	0.70	48.42
Butyl benzyl phthalate	2.26	57.72
Bis(2-ethylhexyl)phthalate	1.02	58.05
Di-n-octyl phthalate	1.29	58.24
Diisononyl phthalate	0.36	50.97
Diisodecyl phthalate	0.94	60.69

Analytical Conditions

- Instrument: GC-MS in Scan mode w/EIC (35-450 m/z)
- Column: CA-5 capillary column (30 m x 0.25 mm x 0.25 µm)
- Run program:
 - 55 °C x 1 min; 20 °C/min to 200 °C, hold 1 min; 30 °C/min to 310 °C, hold 3 min.
 - Detector: 280 °C & Injector 250 °C
- MS Ions: The primary ion monitored for four of the six phthalates was 149 m/z. Since DINP and DIDP partially co-eluted secondary ions of 293 m/z (DINP) and 307 m/z (DIDP) were used. Bisphenol A was quantitated using 213 m/z.

All samples were spiked with an internal standard (SPEX CertiPrep CLPS-I90) and compared to a standard phthalate mix, prepared at multiple levels to obtain a calibration curve. A BPA standard was also run at multiple levels to create a BPA calibration curve (S-509).

Results

HDPE Toys

Of the two types of plastic toys discussed here, PVC and HDPE, the HDPE toys showed the lowest levels of phthalates. DNOP was detected at levels below 130 µg/g in 5 of the 6 HDPE toys. This level is well below the CPSC limit of 0.1% (1000 µg/g) of DNOP. Bisphenol A was not detected in any of the HDPE toys.

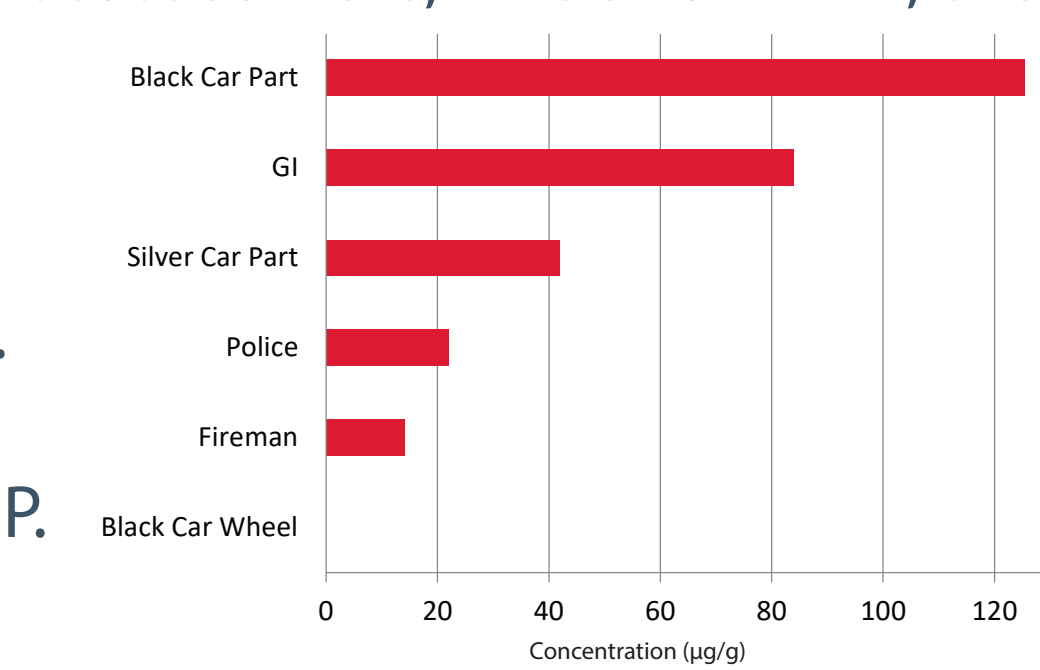


Figure 1. Di-n-octyl phthalate in select HDPE toys

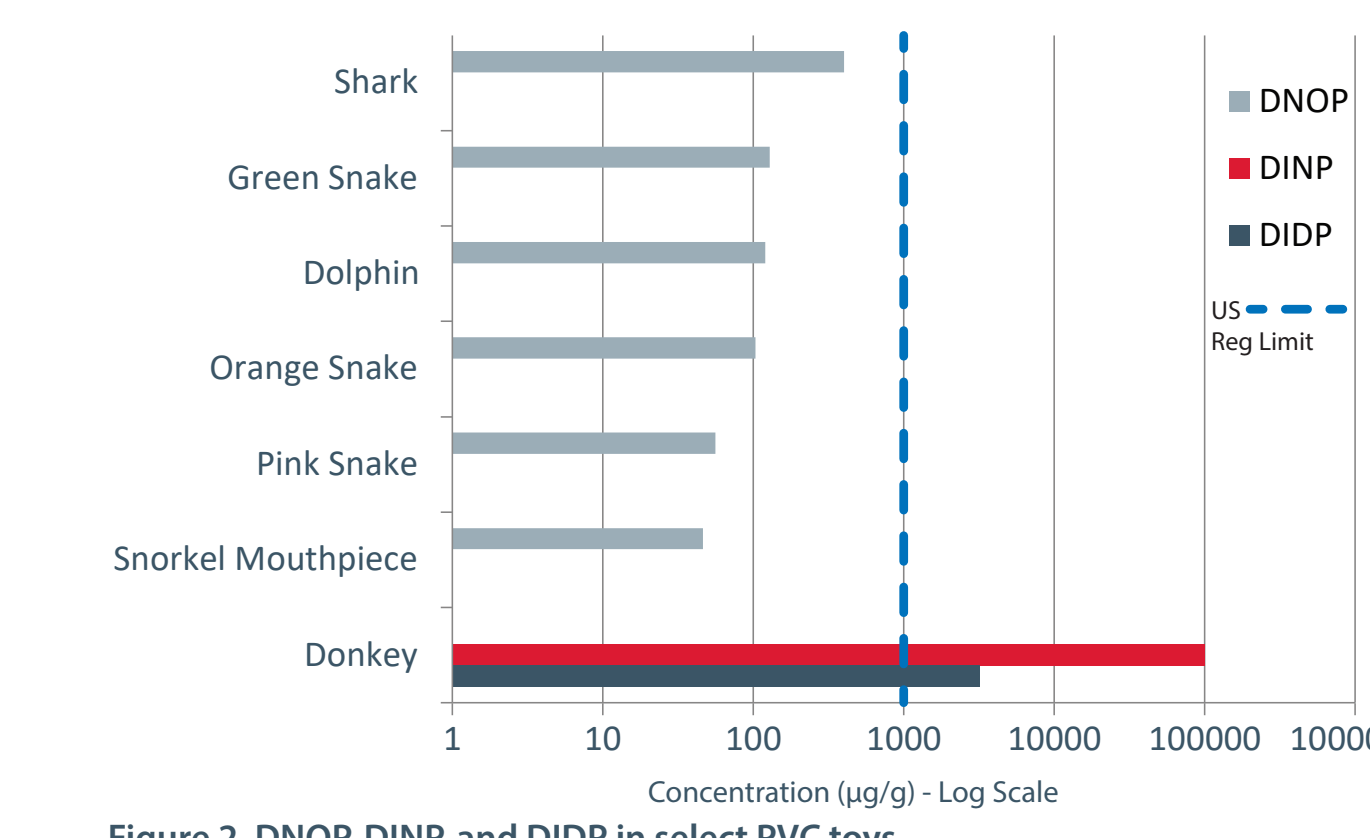


Figure 2. DNOP, DINP, and DIDP in select PVC toys

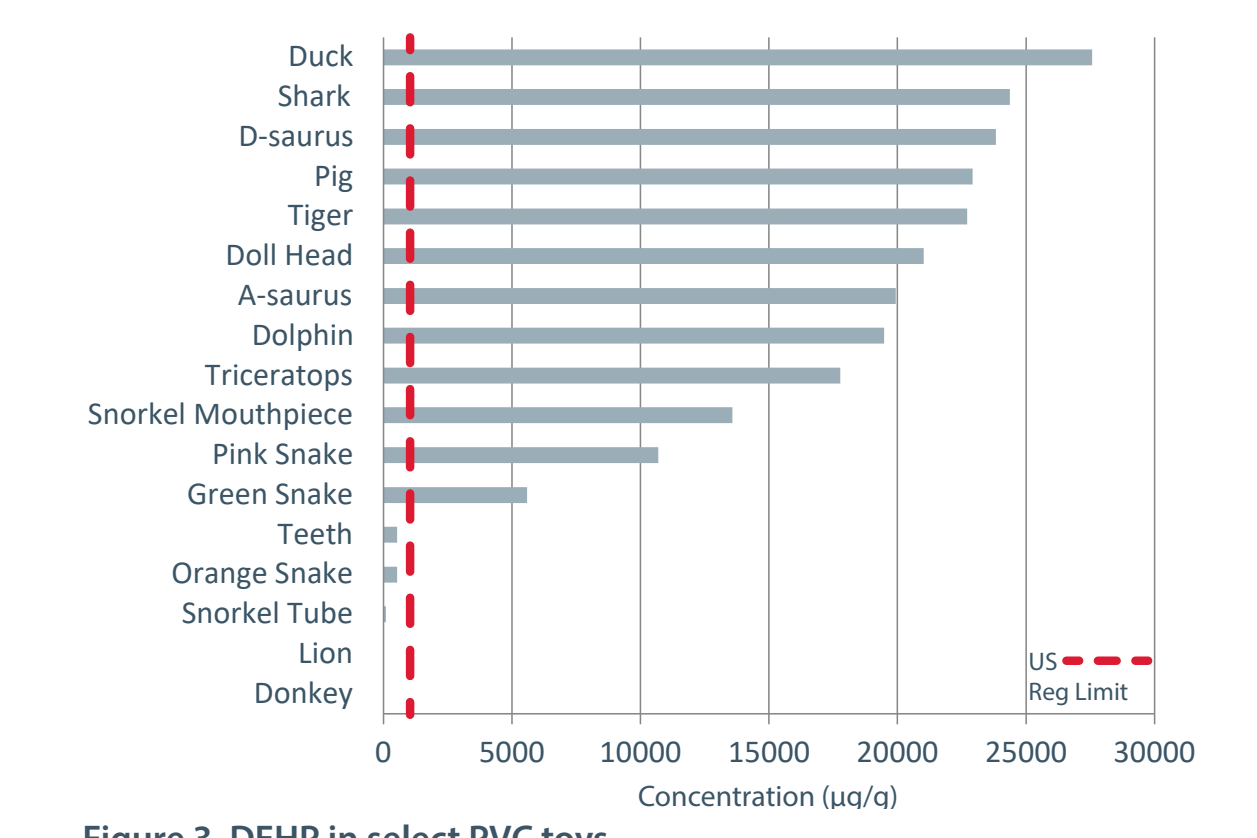


Figure 3. DEHP in select PVC toys

Three other phthalates were found in the PVC toys: DIDP, DINP, and DNOP. The average DNOP level in toys was found to be about 100 µg/g. DIDP and DINP were detected predominantly in the donkey toy where the highest phthalate level overall was detected with 100 µg/g of DINP.

Bisphenol A was detected in four toys. The highest levels of BPA were 1200 µg/g in the fashion doll's head and 700 µg/g in the rubber duck.

The US CPSC method allows for 0.1% by weight of each individual restricted phthalate while the regulations for the EU and Japan call for restrictions of total restricted phthalates below 0.1% by weight. The majority of PVC toys in this study contained a total weight for the six restricted phthalates exceeding both the US regulation and the more stringent EU and Japanese regulations.

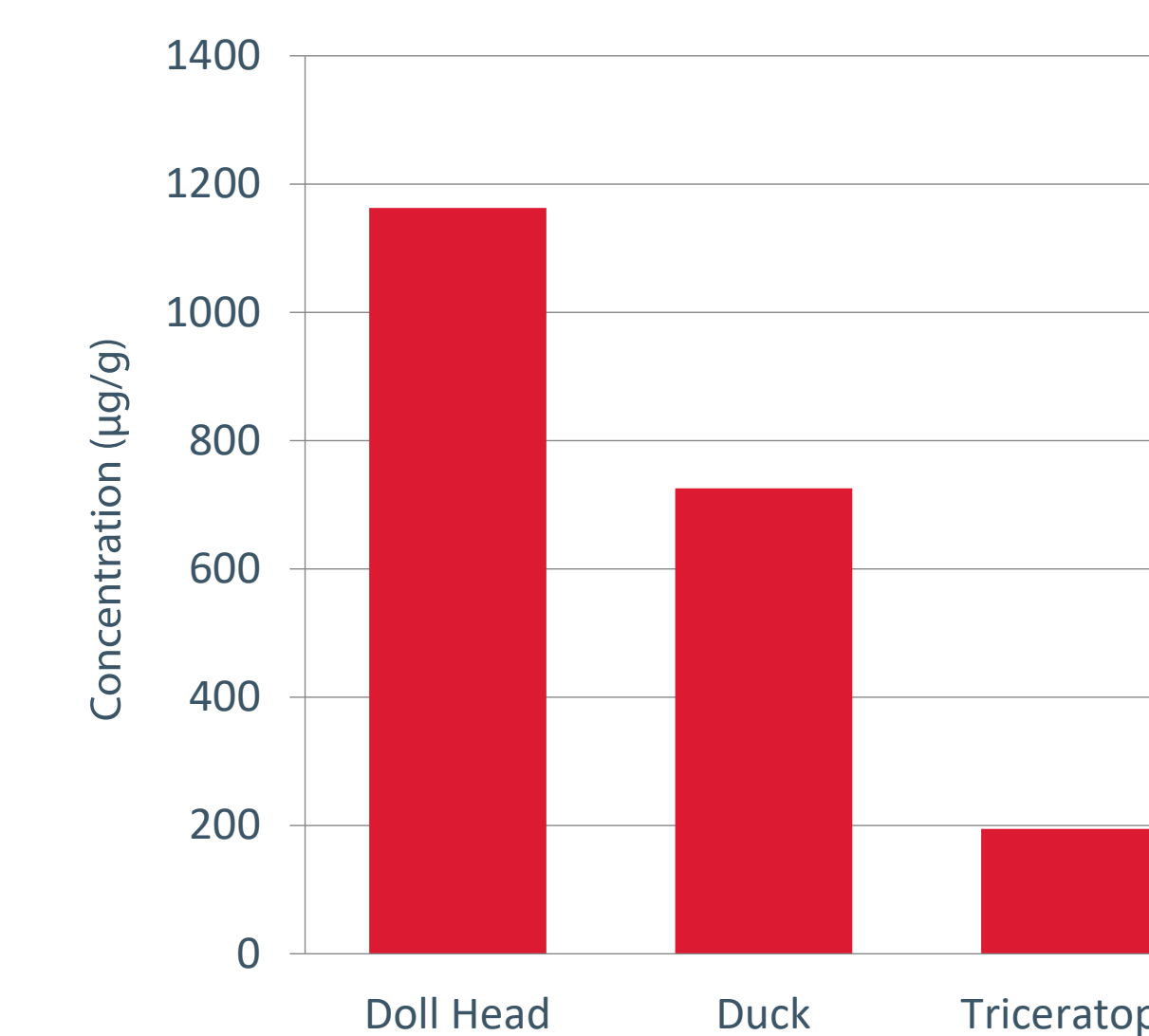


Figure 4. BPA in select toys

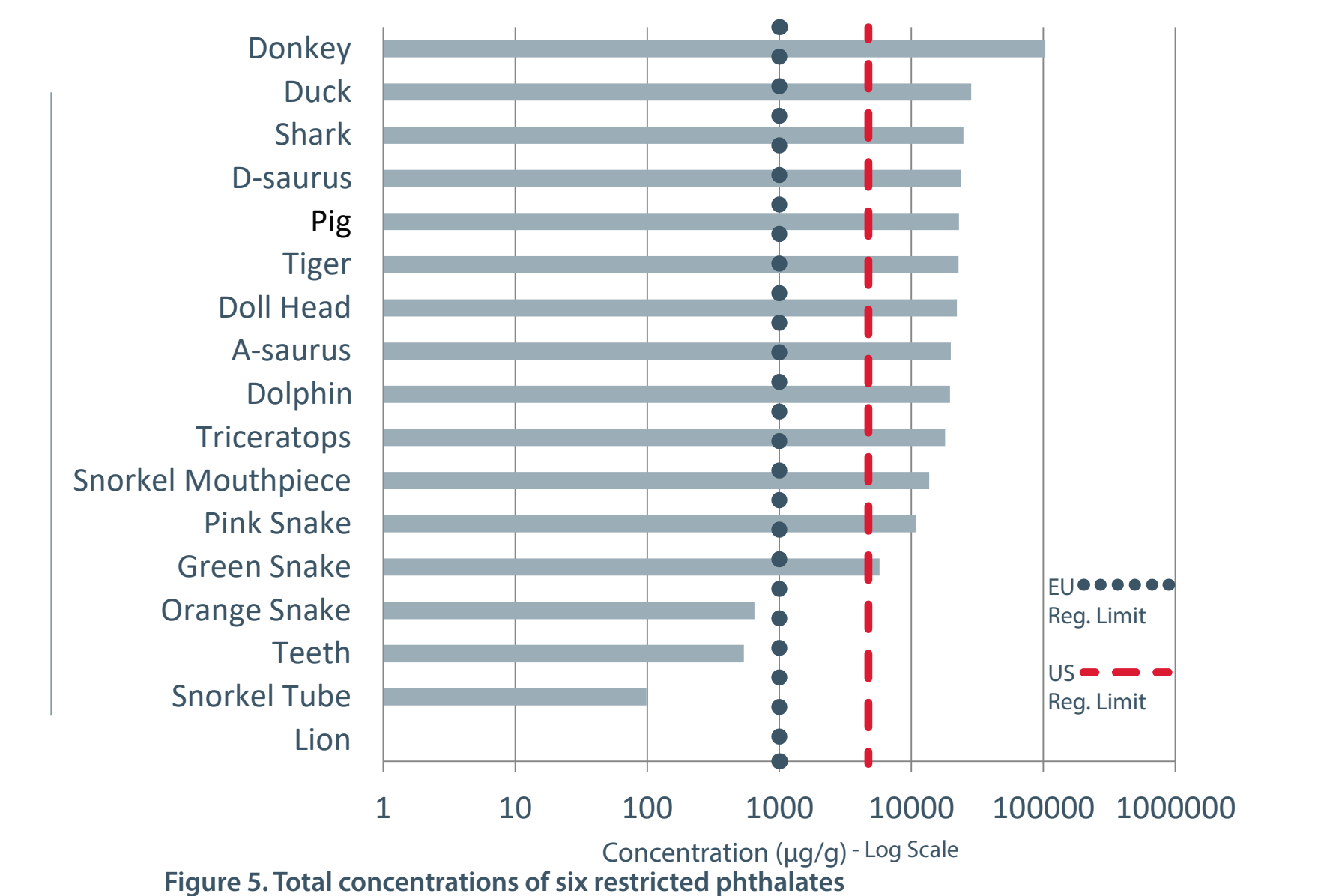


Figure 5. Total concentrations of six restricted phthalates

Conclusions

The PVC toys contained the highest levels of phthalates and Bisphenol A of all the types of plastic tested. The PVC predominately contained DEHP at levels over the current CPSC limits of 0.1%. BPA was found in four of the PVC toys and levels of two of the toys approached or exceeded 1000 µg/g.

Proper sample preparation and extraction is critical to ensuring an accurate recovery of phthalates from the different plastic polymers. Each polymer type requires a different method to achieve an optimized recovery rate. The failure to recognize that one extraction method (primarily the CPSC PVC method) is not suited for different types of polymer could alter the recovery rate and analysis for these restricted phthalates.