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FINAL REPORT

Analysis of Heavy Metals in Cleaning Products

HLA Study No. 6310-101

for

The Soap and Detergent Association
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by

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INTRODUCTION

Samples of household cleaning products (laundry detergent, laundry bleach, fabric softener, and dish detergent) were analyzed for arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc to develop background information on the potential contribution of these products to the heavy metal contamination of municipal sewage. The sample collection was designed to represent the majority of products used, and the analytical samples were prepared as category composites in proportion to their market share. The analytical results are in Table I.

SAMPLE SOURCES, CATEGORIES, AND HANDLING

Samples were collected in three California cities: Palo Alto, San Jose, and Sunnyvale. An attempt was made to collect identical unit sizes of all products in each category, but due to local limitations in product availability, several omissions or substitutions were necessary. These alterations are delineated in the Compositing Procedure Section.

Sampling was conducted by the Nutrition Network, Laguna Beach, California.

Samples were shipped in their original containers to Hazleton Laboratories America, Inc., Madison, Wisconsin, by Federal Express from August 7 through 17, 1989.

Hazleton handled all samples according to the laboratory chain of custody standard operating procedure.

COMPOSITING PROCEDURE

The Soap and Detergent Association provided estimates of the relative market volume shares to be used as a guide in sample compositing (Appendix I). Brand samples within each category were composited based on the relative market shares of each brand in the category.

Three containers of each brand from each of three cities were combined and well mixed. From this composite, a weight was taken based on the market share percentages, and this final composite was well mixed. The weights taken were as follows:

Powder Laundry Detergents	Weight (g)	Percent
Tide®	700	35
Surf®	280	14
All®	180	9
Bold®	160	8
Cheer®	160	8
Purex®	120	6
Arm and Hammer®	100	5
Fresh Start®	100	5
Clorox®	80	4
Dash®	60	3
Tide with bleach	60	3
Gain®	20	1
Oxydol®	20	1
Total	2,040	102

Note: Purex and Dash were not available from Palo Alto. Sunnyvale sent Lemon Fresh Dash; San Jose sent Regular Dash.

Liquid Laundry Detergents	Weight (g)	Percent
Liquid Tide®	500	25
Wisk®	480	24
Liquid All®	340	17
Liquid Cheer®	140	7
Era®	140	7
Liquid Surf®	140	7
Liquid Bold®	120	6
Liquid Arm and Hammer®	120	6
Total	1,980	99

Liquid Bleaches	Weight (g)	Percent
Clorox®	1,420	71
Purex®	340	17
Clorox II®	160	8
Vivid®	60	3
Total	1,980	99

Note: No Vivid was available from Palo Alto.

Powdered Bleaches	Weight (g)	Percent
Clorox II®	1,060	53
Biz®	680	34
Borateem®	280	14
Total	2,020	101

Liquid Fabric Softeners	Weight (g)	Percent
Downy® (Regular)	1,080	54
Snuggle®	560	28
Downy® (Sun Rinse)	360	18
Total	2,000	100

Liquid Hand Dishwashing Detergents	Weight (g)	Percent
Palmolive Liquid®	380	19
Dawn®	300	15
Ivory Liquid®	280	14
Crystal White Octagon®	280	14
Joy®	280	14
Sunlight®	260	13
Dove®	200	10
Total	1,980	99

Note: Ivory Liquid was not available from Palo Alto. The Nutrition Network substituted White Magic by Safeway, but this was not included in the composite because it was not a part of the study protocol.

Liquid Automatic Dishwashing Detergents	Weight (g)	Percent
Cascade®	740	37
Palmolive Liquid®	640	32
Sunlight Liquid®	600	30
Total	1,980	99

Note: Cascade from Sunnyvale, Palmolive Liquid from San Jose, and Sunlight Liquid from Sunnyvale were Lemon Scent. All others were Regular Scent. Palo Alto mistakenly sent Sunlight Liquid hand dishwashing detergent. This mistake was discovered during the composite preparation stage. Therefore, the mix was terminated and restarted. The loss of the first mix resulted in

a shortage of the San Jose Sunlight. The difference was made up with Sunnyvale Sunlight. To summarize, the final composite consisted of 1/4 San Jose to 3/4 Sunnyvale, as opposed to 1/3 San Jose to 1/3 Sunnyvale to 1/3 Palo Alto. Sunlight was represented correctly, but the proportion from each city was different.

Powdered Automatic Dishwashing Detergents	Weight (g)	Percent
Cascade®	1,400	70
Sunlight®	360	18
Electrosol®	220	11
Total	1,980	99

Note: Cascade from Sunnyvale and Sunlight from all three cities were Lemon Scent. All others were Regular Scent.

MATERIALS

Reagents

- Water, double deionized
- Nitric acid, GR grade, EM Science, Gibbstown, New Jersey, NX0409-7
- Sulfuric acid, GR grade, EM Science, SX1244-5
- Sodium borohydride, Fisher Scientific, Fairlawn, New Jersey, S678-25
- Stock solutions of metallic elements, 1,000 ppm, Fisher Scientific

Equipment

- General laboratory glassware
- Filter paper, Fisher P8, coarse, 15.0 cm, 09-795F, Fisher Scientific

Instrumentation

- Spectrometer, Atomic Absorption, Perkin-Elmer Model 5000
- Mercury/hydride system, Perkin-Elmer MHS-20

SAMPLE PREPARATION AND ANALYSIS

Sample sizes and initial dilution volumes are summarized in Table II.

Several of the products and composite samples were observed to be heterogeneous, thus precautions were taken to assure that homogenous aliquots were prepared for

analysis. Powder-type samples were prepared for compositing as follows: the whole-package contents of identical brands from each of the three cities were combined and physically homogenized with a Hobart® A-200 grinder. After composite preparation, the composite was again ground with the Hobart grinder before bottling.

The liquid bleach and liquid laundry detergent composites commonly separated after approximately 24 hours. The detergent was rehomogenized by shaking. The bleach was rehomogenized by processing with a Polytron®.

The liquid bleach was accidentally contaminated with copper when it was processed with the Polytron. Therefore, the bleach was recomposited as follows on August 31, 1989, after which it was weighed immediately and prepared for copper reanalysis.

Liquid Bleaches	Weight (g)	Percent
Clorox	355	71
Purex	85	17
Clorox II	40	8
Vivid	15	3
Total	495	99

Copper, Cadmium, Chromium, Lead, Nickel, and Zinc

The powdered laundry detergents, liquid laundry detergents, powdered bleaches, liquid automatic dishwashing detergents, and powdered automatic dishwashing detergents were digested with nitric acid in beakers on a hot plate and transferred to 50-mL volumetric flasks and filtered.

The liquid bleaches, liquid fabric softeners, and liquid hand dishwashing detergents were pre-ashed on hot plates, and then ashed at 500° for 10 hours.

All six of these elements were determined on the same digest by flame atomic absorption spectroscopy. Instrument operating parameters are summarized in Appendix II.

Silver

The powdered laundry detergents, liquid laundry detergents, powdered bleaches, and liquid and powdered automatic dishwashing detergents were digested with nitric acid in beakers on a hot plate. The samples were filtered as with the above digests.

The liquid bleaches, liquid fabric softeners, and liquid hand dishwashing detergents were pre-ashed on hot plates, and then ashed at 500° for 10 hours.

Digestates were analyzed by flame atomic absorption spectroscopy. Instrument operating parameters are summarized in Appendix II.

Mercury

The samples were digested with a mixture of sulfuric and nitric acids. The mercury was reduced with sodium borohydride by the Perkin-Elmer MHS-20 Hydride System. Instrument operating parameters are summarized in Appendix II.

Arsenic

The samples were digested with a mixture of sulfuric and nitric acids. The arsenic was converted to arsine by the Perkin-Elmer MHS-20 Hydride System. Instrument operating parameters are summarized in Appendix II.

PREPARATION OF SAMPLE SPIKES

For all analytes, the samples were spiked and digested as previously discussed. The choice of spiking levels depended upon the analyte concentrations determined in the unspiked samples. For analytes found to be less than the detection limit, the spike level addition was calculated as four times the respective detection limit. For samples with quantifiable analyte levels, spikes were added at five times the levels found. Table III summarizes the analyte additions used to formulate the spiked samples. Table IV summarizes the analytical spike recovery data.

METHOD REFERENCES

Mercury

- Digestion: Analyst, 86:608, (1961) (with modifications).
- Determination: Analytical Chemistry, 40:2085 (1968).

Arsenic

- Digestion: Analytical Methods Committee, Analyst, 85:643-656 (1960).
- Analytical Methods Using the MHS Mercury/Hydride System, Perkin-Elmer: Norwalk, Connecticut (January 1981).

Cadmium

- Official Method of Analysis, 14th Ed., Methods 25.061-25.065, 33.089-33.094, AOAC: Arlington, Virginia (1984).
- Friend, M. T., Smith, C. A., and Wishart, D., Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer: Norwalk, Connecticut (January 1982).
- Atomic Absorption Newsletter, 16(2):46-49 (1979) (modified).
- Methods for Chemical Analysis of Water and Wastes, Metals 1-19 and Method 213.1, U.S. EPA: Cincinnati, Ohio (1979).

Chromium

- Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer: Norwalk, Connecticut (January 1982).
- Methods for Chemical Analysis of Water and Wastes, Metals 1-19 and Method 218.1, U.S. EPA: Cincinnati, Ohio (1979).

Copper

- Official Method of Analysis, 14th Ed., Methods 2.126-2.130, 7.096-7.100, 43.A37-43.A40, 49.A01-49.A04, AOAC: Arlington, Virginia (1984).

Lead

- Official Method of Analysis, 14th Ed., Methods 25.089-25.094, 33.089-33.094, AOAC: Arlington, Virginia (1984) (samples with less than 4.00 ppm of lead).
- Official Method of Analysis, 14th Ed., Methods 25.104-25.109, AOAC: Arlington, Virginia (1984) (samples with greater than 4.00 ppm of lead).
- Test Methods for Evaluating Solid Waste, EPA Publication No. SW-846, 2nd Ed., Methods 3030, 3040, or 3050 and 7421, U.S. EPA: Washington, D.C. (Revised April 1984).

Silver

- Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer: Norwalk, Connecticut (January 1982).
- Methods for Chemical Analysis of Water and Wastes, Metals 1-19 and Method 272.1, U.S. EPA: Cincinnati, Ohio (1979).

Nickel

- Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer: Norwalk, Connecticut (January 1982).
- Methods for Chemical Analysis of Water and Wastes, Metals 1-19 and Method 249.1, U.S. EPA: Cincinnati, Ohio (1979).

Zinc

- Official Method of Analysis, 14th Ed., Methods 2.126-21.130, 7.096-7.100, 25.175-25.178, 43.A37-43.A40, AOAC: Arlington, Virginia (1984).

RESULTS AND DISCUSSION

The analytical results of nine heavy metal determinations performed on eight composited samples are summarized in Table I. Each composite was analyzed in duplicate, denoted by either Result 1 or Result 2. Agreement between the duplicates in all cases was good (less than 20% relative percent difference). As a rule, zinc had the widest variation. Values for chromium, mercury, nickel, and silver were lower than the contract-required detection limit (CRDL). One composite contained lead at a concentration greater than the CRDL. Generally, liquid cleaning products had lower heavy metal content than powdered cleaning products, with the exception of the liquid automatic dishwashing detergents.

The values of the analytical spike recoveries (Table IV) ranged from 77% to 122%, with the total average of 98.3%.

SIGNATURES

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(6310-101/sgf)

Table I

Analytical Results - Heavy Metal Determinations
in Household Cleaning Products

Product	Analyte Concentration (mg/kg)								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Ag	Zn
Powder Laundry Detergent									
Result 1 90803280	13.8	0.28	<1	0.49	<0.2	<0.025	<0.5	<0.5	6.82
Result 2 90803281	13.8	0.25	<1	0.49	<0.2	<0.025	<0.5	<0.5	7.72
Liquid Laundry Detergent									
Result 1 90803284	0.022	<0.2	<1	0.21	<0.2	<0.025	<0.5	<0.5	1.16
Result 2 90803285	0.024	<0.2	<1	0.21	<0.2	<0.025	<0.5	<0.5	1.16
Liquid Bleach									
Result 1 90802388	0.005	<0.2	<1	<0.2	<0.2	<0.025	<0.5	<0.5	3.12
Result 2 90803289	0.005	<0.2	<1	<0.2	<0.2	<0.025	<0.5	<0.5	2.65
Powder Bleach									
Result 1 90803292	21.2	0.72	<1	0.30	<0.2	<0.025	<0.5	<0.5	5.23
Result 2 90803293	18.8	0.72	<1	0.30	<0.2	<0.025	<0.5	<0.5	4.78
Liquid Fabric Softener									
Result 1 90803296	0.010	<0.2	<1	<0.2	<0.2	<0.025	<0.5	<0.5	<0.5
Result 2 90803297	0.012	<0.2	<1	<0.2	<0.2	<0.025	<0.5	<0.5	<0.5
Liquid Hand Dish Detergent									
Result 1 90803300	0.012	<0.2	<1	<0.2	<0.2	<0.025	<0.5	<0.5	<0.5
Result 2 90803301	0.014	<0.2	<1	<0.2	<0.2	<0.025	<0.5	<0.5	<0.5
Liquid Automatic Dish Detergent									
Result 1 90803304	6.75	0.37	<1	0.49	0.34	<0.025	<0.5	<0.5	7.72
Result 2 90803305	6.50	0.37	<1	0.59	0.39	<0.025	<0.5	<0.5	7.95
Powder Automatic Dish Detergent									
Result 1 90803308	17.5	1.06	<1	2.40	<0.2	<0.025	<0.5	<0.5	9.31
Result 2 90803309	20.0	1.06	<1	2.40	<0.2	<0.025	<0.5	<0.5	9.08

Table II

Sample Preparation Specifications - Heavy Metal Determinations in Cleaning Products

Element	Sample Weight (g)	Initial Dilution Volume (mL)
Arsenic	1.00	25.0
Cadmium	5.00	50.0
Chromium	5.00	50.0
Copper	5.00	50.0
Lead	5.00	50.0
Mercury	2.00	100.0
Nickel	5.00	50.0
Silver	5.00	50.0
Zinc	5.00	50.0

Table III

Analytical Spike Additions - Heavy Metal Determinations in Household Cleaning Products

Product	Analyte Added (µg)[a]								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Ag	Zn
Power Laundry Detergent 90803282	50	2.0	20	3.0	4.0	0.20	10	10	40
Liquid Laundry Detergent 90803286	0.10	4.0	20	2.0	4.0	0.20	10	10	6.0
Liquid Bleach 90803290	0.02	4.0	20	4.0	4.0	0.20	10	10	70
Powder Bleach 90803294	62.5	4.0	20	2.0	4.0	0.20	10	10	30
Liquid Fabric Softener 90803298	0.05	4.0	20	4.0	4.0	0.20	10	10	10
Liquid Hand Dish Detergent 90803302	0.05	4.0	20	4.0	4.0	0.20	10	10	10
Liquid Automatic Dish Detergent 90803306	25	2.0	20	3.0	2.0	0.20	10	10	40
Powder Automatic Dish Detergent 90803310	80	5.0	20	15	4.0	0.20	10	10	50

a Refer to Table II for sample weights and dilution volumes.

Table IV

Analytical Spike Recoveries - Heavy Metal Determinations
in Household Cleaning Products

Product	Recovery (Percent)								
	As	Cd	Cr	Cu	Pb	Hg	Ni	Ag	Zn
Power Laundry Detergent 90803282	82	120	108	92	122	93	95	101	103
Liquid Laundry Detergent 90803286	91	95	108	98	104	77	111	101	123
Liquid Bleach 90803290	80	95	108	111	86	112	111	97	107
Powder Bleach 90803294	88	95	108	108	115	93	111	90	98
Liquid Fabric Softener 90803298	94	95	82	104	79	90	111	100	86
Liquid Hand Dish Detergent 90803302	84	95	92	79	90	86	95	100	109
Liquid Automatic Dish Detergent 90803306	104	98	108	83	81	109	111	94	102
Powder Automatic Dish Detergent 90803310	78	90	92	94	122	98	111	101	92

APPENDIX I

Product Brands to be Collected and Composited

Brand	Manufacturer	Market Share	Cumulative Share	Weighting Factor
Powder Laundry Detergents				
Tide	Procter & Gamble	28	28	35
Surf	Lever Brothers	11	39	14
All	Lever Brothers	7	46	9
Bold	Procter & Gamble	6	52	8
Cheer	Procter & Gamble	6	58	8
Purex	Dial	5	63	6
Arm & Hammer	Church & Dwight	4	67	5
Fresh Start	Colgate-Palmolive	4	71	5
Clorox	Clorox	3	74	4
Dash	Procter & Gamble	2	76	3
Tide w/Bleach	Procter & Gamble	2	78	3
Gain	Procter & Gamble	1	79	1
Oxydol	Procter & Gamble	1	80	1
Liquid Laundry Detergents				
Liquid Tide	Procter & Gamble	21	21	25
Wisk	Lever Brothers	20	41	24
Liquid All	Lever Brothers	14	55	17
Liquid Cheer	Procter & Gamble	6	61	7
Era	Procter & Gamble	6	67	7
Liquid Surf	Lever Brothers	6	73	7
Liquid Bold	Procter & Gamble	5	78	6
Liquid Arm & Hammer	Church & Dwight	5	83	6
Liquid Bleach				
Clorox	Clorox	45	45	71
Purex	Dial	11	56	17
Clorox II	Clorox	5	61	8
Vivid	---	2	63	3
Powdered Bleach				
Clorox II	Clorox	42	42	53
Biz	Procter & Gamble	27	69	34
Borateem	Dial	11	80	14

APPENDIX I (Continued)

Product Brands to be Collected and Composited

Brand	Manufacturer	Market Share	Cumulative Share	Weighting Factor
	Liquid Fabric Softener			
Downy (Regular)	Procter & Gamble	44	44	54
Snuggle	Lever Brothers	23	67	28
Downy (Sun Rise)	Procter & Gamble	15	82	18
	Liquid Hand Dishwashing Detergent			
Palmolive Liquid	Colgate-Palmolive	16	16	19
Dawn	Procter & Gamble	13	29	15
Ivory Liquid	Procter & Gamble	12	41	14
Crystal White Octagon	---	12	53	14
Joy	Procter & Gamble	12	65	14
Sunlight	Lever Brothers	11	76	13
Dove	Lever Brothers	8	84	10
	Liquid Automatic Dishwashing Detergent			
Cascade	Procter & Gamble	37	37	37
Palmolive Liquid	Colgate-Palmolive	32	69	32
Sunlight Liquid	Lever Brothers	30	99	30
	Powdered Automatic Dishwashing Detergent			
Cascade	Procter & Gamble	58	58	70
Sunlight	Lever Brothers	15	73	18
Electrosol	Benckiser	9	82	11

APPENDIX II

Instrument Parameters
Atomic Absorption

Element	Technique	Instrument	Analytical Wavelength (nm)	Slit (nm)	Gases	Standard Solutions (Range) (ppm)
Arsenic	Hydride	PE 5000/MHS-20	193.7	0.7	Argon (carrier)	0.0 - 0.030
Cadmium	Flame	PE 5000	228.8	0.7	Air/acetylene	0.02 - 1.0
Chromium	Flame	PE 4000	357.9	0.7	N_2O/acetylene	0.1 - 3.0
Copper	Flame	PE 4000	324.7	0.7	Air/acetylene	0.02 - 1.0
Lead	Flame	PE 4000	283.3	0.7	Air/acetylene	0.0 - 3.0
Mercury	Hydride	PE 5000/MHS-20	253.7	0.7	Argon (carrier)	0.0 - 0.050
Nickel	Flame	PE 5000	232.2	0.2	Air/acetylene	0.05 - 5.0
Silver	Flame	PE 4000	328.1	0.7	Air/acetylene	0.05 - 1.0
Zinc	Flame	PE 5000	213.9	0.7	Air/acetylene	0.05 - 3.0

PE Perkin-Elmer Corp., Norwalk, CT

MHS-20• Perkin-Elmer Mercury/Hydride System