THE CONTRIBUTION OF HEAVY METALS TO WASTEWATERS FROM HOUSEHOLD CLEANING PRODUCTS

prepared for the

Soap and Detergent Association

July 1990

prepared by
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Soap and Detergent Association
475 Park Avenue South
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ATTN: Mr. Richard Sedlak
Research Director

Subject: Final report on the Contributions of Heavy Metals to Wastewaters from Household Cleaning Products

Dear Mr. Sedlak:

In accordance with our agreement, we are submitting our report on **The Contributions of Heavy Metals to Wastewaters from Household Cleaning Products**. The report provides a comprehensive overview of the data available in the world wide literature along with an in-depth review of recent wastewater heavy metals loadings determinations conducted in the San Francisco Bay Area.

This report was prepared by Dr. David Jenkins with assistance from me. The report summarizes our literature search and review on heavy metals content in municipal sewage and cleaning products with emphasis on arsenic, cadmium, copper, chromium, lead, mercury, nickel, and zinc.

Respectfully submitted,

RUSSELL ENVIRONMENTAL ENGINEERING AND DEVELOPMENT (REED) CORPORATION

Larry L. Russell, Ph.D.,P.E.
President

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Executive Summary

The contribution from various sources including household cleaning products, other residential wastewater, water supply and permitted industry to the heavy metals in influent wastewater and treated effluent were determined for the wastewater treatment plants of San Jose/Santa Clara, Palo Alto and Sunnyvale, which are located in the Southern San Fransisco Bay Area of California. Heavy metals contributions from these sources were determined and compared to their respective current and proposed National Pollution Discharge Elimination System (NPDES) permit limits.

The heavy metals studied were arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc. In no case were household cleaning products the major heavy metal contributor to influent wastewater or wastewater effluents. The highest heavy metal contribution from household cleaning products was for arsenic, which respectively accounted for 73 percent of the residential contribution, 13 percent of the influent and effluent wastewater content but only 5 percent and 3 percent of the current and proposed NPDES permit limits. All other household cleaning product heavy metals contributions to influent and effluent wastewater and to current and proposed discharge limits were below 1 percent of the total metal present.

Objective

The overall objective of this study was to determine the contribution of heavy metals to wastewaters from household cleaning products. Due to recent revisions to the NPDES discharge requirements to San Francisco Bay and especially for the shallow Southern San Francisco Bay the study location was defined as the Southern San Francisco Bay Area, specifically the area tributary to the wastewater treatment plants at San Jose/Santa Clara, Palo Alto, and Sunnyvale, California. These wastewater treatment plants serve a total population of approximately 1.2 million people.

Approach

This project involved the determination of the fractional contribution of heavy metals from identifiable sources, to the total influent municipal wastewater heavy metals loading, to the effluent heavy metals loading, and to the current and proposed heavy metals discharge standards. In addition, the heavy metals contribution from the residential component of the influent wastewater was determined.

The study involved the following:

(i) a comprehensive literature review of existing data on heavy metals contents of household cleaning products, residential wastewater and municipal wastewater;

(ii) use survey and sampling and analysis of selected household cleaning products;

(iii) review of heavy metals loadings and their source categories in the influent to the San Jose/Santa Clara, Palo Alto and Sunnyvale wastewater treatment plants;

(iv) determination of the "net residential" (residential minus water supply) heavy metals loadings;

(v) determination of the influent municipal wastewater minus permitted industrial heavy metals loading;

(vi) determination of the heavy metals loadings in the effluents from the San Jose/Santa Clara, Palo Alto and Sunnyvale wastewater treatment plants; and

(vii) preparation of a report identifying the contribution of household cleaning products to the heavy metals loads in 1) influent municipal wastewater 2) the wastewater effluent 3) the current and future proposed effluent NPDES limits and 4) the net residential wastewater.

Items (i) and (vii) were conducted by the authors; item (ii) was performed by the Nutrition Network, Laguna Beach, CA (sampling) and Hazelton Laboratories America, Inc., Madison, WI (compositing and heavy metals analysis); items (iii) and (vi) were obtained from reports prepared by CH2M Hill, Inc., Emeryville, CA (for the San Jose/Santa Clara plant), J.M. Montgomery Engineers, Inc., Walnut Creek, CA (for the Palo Alto plant), and Eisenberg and Olivieri and Associates, Inc., Oakland, CA (for the Sunnyvale plant); items (iv) and (v) were calculated by the authors from data collected by the organizations listed in (iii) for the three treatment plants studied.

Literature Review—Heavy Metals Contributions to Wastewater

In this study, heavy metals contributions generally are expressed in terms of a per capita mass loading with the units of mg/capita/day. In cases where it was not possible to reliably determine per capita mass loading (e.g. for historical data on household cleaning product heavy metals contents) concentration data were reported.

For the purposes of this study the source categories for heavy metals in the influent wastewater are identified as follows:

(i) water supply -- those heavy metals present in the municipal water supply,

(ii) domestic contribution -- those heavy metals contributed by residential water usage excluding the heavy metals contribution from the water supply,

(iii) permitted industry -- those heavy metals contributed by industries defined by the EPA Pretreatment Program or the local agency as significant discharges or categorical industries.

(iv) non-permitted industry -- those heavy metals contributed by industries which are regulated by local limits established under the EPA Pretreatment Regulations,

(v) commercial activities -- those heavy metals contributed by commercial establishments and businesses,

(vi) infiltration and inflow -- those heavy metals contributed by infiltration and inflow into the sewer system.

For the purpose of this study, the seasonal variation due to infiltration was assumed to be negligible.

The literature review produced 15 references in which the influent municipal wastewater loads of heavy metals exclusive of contributions from permitted industries were presented, or could be derived. Table 1 presents a summary of this data, and a computation of ranges and average values. Again these data represent the total municipal wastewater with only the "permitted industry category" (where known) excluded; therefore they should not be construed as residential contribution data.

It is essential to read the information in the footnotes of Table 1 to understand the sources and conditions under which the data were obtained, and the assumptions and calculations which were required to express the heavy metals contributions on a per capita basis. Where no specific sewage flow data were available to compute per capita heavy metals loading from heavy metals concentration data, it was assumed that the domestic sewage flow was 100 gal/capita/day.

A review of the literature turned up a few instances where just the residential contribution of heavy metals could be determined. Most of the data available were for "domestic sewage" which certainly contained heavy metals contributions from the water supply (due to corrosion, addition of corrosion control products and other natural phenomena), and likely also from non-permitted industries and commercial activities. The available data for "net residential" contribution (residential contribution less the heavy metals contribution from the water supply) are presented in Table 2, together with the range and average of the available data.

Similarly, very little data were available on the heavy metals content of household cleaning products. The information obtained is presented in Table 3. The data in Table 3 are expressed on a "concentration in the product basis" because of the difficulties in calculating the per capita usage rates. The types of products analyzed are indicated in the footnotes.

TABLE 1

LITERATURE REVIEW VALUES FOR INFLUENT MUNICIPAL WASTEWATER HEAVY METALS LOADS EXCLUSIVE OF HEAVY METALS FROM PERMITTED INDUSTRIES

(mg/capita/day)

Metal	Study No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Range of all data[a]	Average of all data[a]
Cd	7.3	5.0	2.7	0.2	3.3	0.8	0.4	2.3	1.7	2.0	0.6	<7	<6	<10	0.6	0.25	0.054	0.10	0.054-7.3	1.9
Cr_T	36	8.3	3.2	3.9	4.6	2.2	1.7	31	8.8	0.1	6	<7	<12	<20	9.1	1.4	0.60	0.53	0.1-36	7.8
Cu	83	45	45	11	27	3.9	33	68	46	-	30	<7	20	81	79	18	2.8	3.3	2.8-83	37
Pb	-	28	45	6.1	15	3.7	9.5	44	12	-	50	<7	<6	<10	-	5.0	1.6	0.71	0.71-50	19
Ni	36	5.4	9.1	3.8	9.9	7.5	6.5	32	18	-	8	15	33	10	28	1.9	0.50	0.45	0.45-36	13
Hg	-	-	-	0.2	0.2	0.1	0.2	-	-	-	0.2	0.03	0.1	0.4	-	-	-	-	0.03-0.4	0.18
Zn	95	77	95	74	46	13	79	180	120	-	100	19	39	40	79	63	27	23	13-180	68

[a]Values of "less than" a certain value were omitted

Source of data for Study No.:

1. New York, NY - Davis and Jacknow (1975)
2. Pittsburg, PA - Davis and Jacknow (1975)
3. Muncie, IN - Davis and Jacknow (1975)
4. Federal Republic of Germany - Nolte (1985)
5. Martinez, CA - Montgomery Engineers (1985)
6. Oakdale, IL - Gurnham and Associates (1979)
7. Hanover Park, IL - Gurnham and Associates (1979)
8. San Francisco, CA - L. Walker and Associates (1987)
9. San Jose, CA - L. Walker and Associates (1987)
10. East Bay Municipal Utilities District, Oakland, CA - L. Walker and Associates (1987)
11. Federal Republic of Germany - ATV (1982)
12. Elmvale, Ontario, Canada - Atkins et. al. (1978)
13. Shelburn, Ontario, Canada - Atkins et. al. (1978)
14. Burlington, Ontario, Canada - Atkins et. al. (1978)
15. New York, NY - Klein et. al. (1974)
16. Yokosuka, Japan - Moriyama et. al. (1989)
17. Hachinohe, Japan - Moriyama et. al. (1989)
18. Hakodate, Japan - Moriyama et. al. (1989)

Explanation of Data in Table 1:

Study No.	
1.2. and 3.	Data given in cited paper as "residential contributions" were used.
4.	Calculated directly from heavy metals load (domestic + small industry) and population given in cited paper.
5.	Total heavy metals load from Central Contra Costa Sanitary District (Table 1 in cited report) minus industrial metals load (Table 9 in cited report) divided by population (assumed 100 gal sewage/cap/day and 36.4 MGD sewage flow).
6. and 7.	Data calculated in cited report.
8.9. and 10.	Figures VII-2, VII-3 and VII-4 in cited report give total and industrial heavy metals contributions. Industrial contributions were subtracted from total contributions and divided by a per capita sewage contribution of 100 gal/cap/day. Tributary populations were obtained from sewage flows.
11.	Data given in cited report for heavy metals.
12.13. and 14.	Data given in cited report for heavy metals concentration, flow and population; solely domestic wastewater systems.
15.	Data given in Table II of paper for residential wastewater was averaged on a flow-weighted basis and 100 gal/cap/day sewage flow assumed.
16.17.and 18.	Data given in Table 3 of paper for influent domestic sewage.

TABLE 2

NET RESIDENTIAL (RESIDENTIAL MINUS WATER SUPPLY) HEAVY METALS CONTRIBUTIONS

(mg/cap/day)

	Study No.							
Metal	1[a]	2[a]	3[b]	4[c]	5[c]	Range of Data	Average of Data	Average of Data from Current Study[d]
As	-	-	-	-	-	-	-	-
Cd	0.33	0.33	2.2	0.15	0.059	0.059-2.2	0.61	0.21
Cr_T	1.1	1.1	1.3	0.56	0.33	0.33-1.3	0.88	0.56
Cu	2.5	1.9	1.2	47	3.6	1.2-47	11	11
Pb	1.9	6.1	-	3.6	2.5	1.9-6.1	3.5	1.8
Hg	3.8	1.1	-	-	-	1.1-3.8	2.4	0.14
Ni	0.02	0	1.1	1.3	0.32	0-1.3	0.54	0.47
Ag	-	-	-	-	-	-	-	-
Zn	0.61	57	1.6	41	19	0.61-57	24	110

[a]Gurnham et al. (1979)
[b]Calculated from Klein et al. (1974)
[c]Moriyama et al. (1989)
[d]See Table 14 this report

Source of data for Study No.:

1 Oakdale, IL
2 Hanover Park, IL
3 New York City, NY
4 Yokosuka, Japan
5 Hachinohe, Japan

TABLE 3

HEAVY METALS CONCENTRATION IN HOUSEHOLD CLEANING PRODUCTS
(mg/kg dry weight of product)
(ppm)

Metal	Study No. 1[c]	2	3	4	5	6	7
Cd	0.007-1.1	-	-	-	-	-	0.55-1.9[a] 0.44-0.52[b]
Cr_T	<0.01-0.66	-	3-9.2[a] 0.4-1.4[b]	-	0.34[a] 0[b]	<1.0-2.9	11-12[a] 1.5-2.1[b]
Cu	0.01-5.1	-	-	-	-	-	9.2-17[a] 1.1-2.0[b]
Pb	<0.002-0.019	-	-	-	-	-0.41-2.4[a]	0.45-0.77[b]
Ni	0.03-22.5	2-9	3.8-7.2[a] 0.7-2.0[6]	0.17-0.89	-	<1.0-5.7	450-700[a] 15-29[b]
Hg	-	-	-	-	-	-	0.005-0.025[a] 0.001-0.008[b]
Zn	1.2-164	-	-	-	-	-	3.0-8.9[a] 3.0-3.6[b]

[a]powder detergents
[b]liquid detergents
[c]"water soluble metals"

Source of data for Study No.:

1 Federal Republic of Germany - Müller (1985); 31 laundry detergents; 1 presoak; 1 decalcifier.
2 The Netherlands - Malten et al. (1964); detergents.
3 Austria - Ebner et al. (1978); powder and liquid detergents.
4 Switzerland - Baselgia (1967); data for 11 synthetic detergents.
5 The Netherlands - Oleffe et al. (1971); powder and liquid detergents.
6 Sweden - Wahlberg et. al. (1977); detergents.
7 U.S.A. - Gurnham and Associates (1979); liquid laundry soap and powder laundry soap.

Assessment of Various Categories of Heavy Metals Inputs to Wastewater Treatment Plants

Three studies have recently been conducted as part of a discharge permit assistance program for the cities of Palo Alto, Sunnyvale and San Jose/Santa Clara wastewater treatment plants. The studies are described in three separate reports respectively by James M. Montgomery Engineers, Inc., Walnut Creek, CA (1989); CH2M Hill, Inc., Emeryville, CA (1989), and Eisenberg Olivieri and Associates, Inc., Oakland, CA (1989).

The details of these studies and their findings will not be discussed here, rather a brief summary of their approaches will be presented. In each case, existing heavy metals concentrations and influent wastewater flow data were used to determine total heavy metals load to the wastewater treatment plants. Then the existing heavy metals concentrations and water usage data were used to determine heavy metals contributions from the water supply. Existing heavy metals concentrations and industrial waste flow data were subsequently used to determine contributions from permitted industries; these contributions were verified by limited field sampling and analysis.

The flows and heavy metals contributions from non-permitted industries, residential sources covering a wide range of socio-economic areas and commercial sources were assessed by sampling programs. The sampling programs for non-permitted industries and commercial sources were conducted individually for each city. The results of sampling and analysis for residential heavy metals contributions for all three cities were pooled.

A common problem, especially with historical data for heavy metals concentrations in water supplies, was that the existing reported concentrations of many heavy metals were below the detection limits for the analytical methods employed. In these situations two assumptions were made: (i) the heavy metal was present at the detection limit concentration and, (ii) the heavy metal concentration was zero. When this situation occurred, the average of these two values was taken for our calculations. To convert the various heavy metals loadings to a per capita basis, it was necessary to know the population tributary to each of the wastewater treatment plants. For Palo Alto the population was 194,000, for Sunnyvale 120,000, and for San Jose/Santa Clara 875,000.

In Table 4, the heavy metals contents of the influent municipal wastewaters less those from permitted industries for the three treatment plants were compared to the range and average of the corresponding data from the literature review presented in Table 1. Contributions of zinc and mercury for San Jose/Santa Clara were above the highest reported literature survey values. The contribution of copper for San Jose/Santa Clara was at the high end of the literature survey values. Perhaps the mercury data reflect the presence of cinnabar (HgS) throughout the Southern San Francisco Bay Area, and the zinc levels reflect the

TABLE 4

COMPARISON OF STUDY AREA INFLUENT MUNICIPAL WASTEWATER MINUS PERMITTED INDUSTRY HEAVY METALS LOADS WITH DATA FROM PREVIOUS STUDIES (mg/cap/day)[b]

Metal	Range of values of previous studies[a]	Average of previous studies[a]	San Jose/ Santa Clara	Palo Alto	Sunnyvale	Flow-weighted average of the three plants
As	-	-	2.3	1.3	2.2	2.1
Cd	0.054-7.3	1.9	3.3	2.2	1.9	3.0
Cr_T	0.1-36	7.8	21	6.2	6.3	17
Cu	2.8-83	37	80	36	50	70
Pb	0.71-50	19	22	8.6	3.3	18
Hg	0.03-0.4	0.18	0.52	0.14	-	0.46[c]
Ni	0.45-36	13	21	1.8	-	17[c]
Ag	-	-	5.0	5.8	0.6	4.7
Zn	13-180	68	220	84	-	190[c]

[a]From Table 1
[b]All data rounded to 2 figures where > 1.0 and to 1 figure where < 1.0
[c]Data for San Jose and Palo Alto only

impact of soft water, the use of zinc orthophosphate as a water distribution system corrosion inhibitor and the silicon industry base.

Assessment of Heavy Metals Contribution by Household Cleaning Products

A product sampling, compositing and analysis program was conducted by Hazelton Laboratories America, Inc. to determine the heavy metals concentrations in a range of household cleaning products that included powder laundry detergents, liquid laundry detergents, liquid bleaches, powder bleaches, liquid fabric softeners, liquid hand dishwashing detergents, liquid automatic dishwashing detergents and powder automatic dishwashing detergents. The specific brand usage data within each of these categories was obtained from a market survey by A. C. Neilsen for the San Francisco and Los Angeles markets (Table 24, Appendix 1). Based on this information a weighting factor was assigned to each of the brands within a product category, and a composite sample representing the usage of the product category was developed (Table 25, Appendix 1). For all products, except liquid bleach (63 percent), this procedure resulted in 80 percent or more of the market share being represented in the composite samples.

Individual brand name samples were collected from retail outlets in 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. The target compositing procedure and any deviations from it are presented in Table 25, Appendix 1.

The analysis of composite cleaning product samples for heavy metals was by atomic absorption spectrophotometry using the pretreatment and analytical methods given in Appendix 2. The analytical results are summarized in Table 5. Each cleaning product composite sample was analyzed in duplicate. The agreement between the duplicates was always good (less than 20 percent relative percent difference). Typically, zinc had the widest variation between duplicates. Values for chromium, mercury, nickel, and silver were all lower than the detection limit. Only one cleaning product composite sample (liquid automatic dishwashing detergent) contained lead at a concentration greater than the detection limit.

The national (USA) average per capita consumption of the various household cleaning products included in the study was determined from product use data obtained by personal communication with some of the companies manufacturing the products studied in combination with published population data. This information is summarized in Table 6 in terms of total annual USA product consumption, and in Table 7 on a per capita basis. The footnotes to these tables describe the sources of the data.

TABLE 5

HEAVY METAL CONCENTRATIONS IN COMPOSITE SAMPLES OF HOUSEHOLD CLEANING PRODUCTS

Product	Analyte Concentration (mg/kg)[a]								
	As	Cd	Cr_T	Cu	Pb	Ni	Hg	Ag	Zn
Powder Laundry Detergent	13.8	0.28	<1	0.49	<0.2	<0.5	<0.025	<0.5	6.82
	13.8	0.25	<1	0.49	<0.2	<0.5	<0.025	<0.5	7.72
Liquid Laundry Detergent	0.022	<0.2	<1	0.21	<0.2	<0.5	<0.025	<0.5	1.16
	0.024	<0.2	<1	0.21	<0.2	<0.5	<0.025	<0.5	1.16
Liquid Bleach	0.005	<0.2	<1	<0.2	<0.2	<0.5	<0.025	<0.5	3.12
	0.005	<0.2	<1	<0.2	<0.2	<0.5	<0.025	<0.5	2.65
Powder Bleach	21.2	0.72	<1	0.30	<0.2	<0.5	<0.025	<0.5	5.23
	18.8	0.72	<1	0.30	<0.2	<0.5	<0.025	<0.5	4.78
Liquid Fabric Softener	0.010	<0.2	<1	<0.2	<0.2	<0.5	<0.025	<0.5	<0.5
	0.012	<0.2	<1	<0.2	<0.2	<0.5	<0.025	<0.5	<0.5
Liquid Hand Dishwashing	0.012	<0.2	<1	<0.2	<0.2	<0.5	<0.025	<0.5	<0.5
Detergent	0.014	<0.2	<1	<0.2	<0.2	<0.5	<0.025	<0.5	<0.5
Liquid Automatic Dishwashing	6.75	0.37	<1	0.49	0.34	<0.5	<0.025	<0.5	7.72
Detergent	6.50	0.37	<1	0.59	0.39	<0.5	<0.025	<0.5	7.95
Powder Automatic	17.5	1.06	<1	2.40	<0.2	<0.5	<0.025	<0.5	9.31
Dishwashing Detergent	20.0	1.06	<1	2.40	<0.2	<0.5	<0.025	<0.5	9.08

[a]Duplicate analyses presented

TABLE 6

ANNUAL USA CONSUMPTION OF THE VARIOUS CLEANING PRODUCT CATEGORIES STUDIED

Product Category	Annual Consumption (million lbs/yr)		
Year	1988-1989[a]	1988[b]	1988[c]
Powdered laundry detergent	3535.2	3109.4	-
Liquid laundry detergent	2330.7	2282.9	-
Powdered machine dishwashing detergent	578.7	514.3	-
Liquid machine dishwashing detergent	215.7	222.5	-
Liquid hand dishwashing detergent	1268.3	1296.5	-
Liquid bleach	-	-	2402
Powdered bleach	-	-	370.4
Liquid fabric softener	1125.1	1212.9	-

[a]Source: Personal communication, Lever Brothers. Market volume for the period August 1988-July 1989.

[b]Source: Personal communication, The Procter & Gamble Company. 1988 market volume.

[c]Source: Personal communication, Clorox. 1988 market volume.

TABLE 7

USA PER CAPITA ANNUAL CONSUMPTION OF THE VARIOUS CLEANING PRODUCTS STUDIED

Product Category	Annual Per Capita Consumption (kg/capita/yr)[d]			
Year	1988-1989[a]	1988[b]	1988[c]	Average of 1988-1989 data
Powder laundry detergent	6.5	5.7	-	6.1
Liquid laundry detergent	4.3	4.2	-	4.3
Powder machine dishwashing detergent	1.1	0.94	-	1.0
Liquid machine dishwashing detergent	0.39	0.41	-	0.4
Liquid hand dishwashing detergent	2.3	2.4	-	2.4
Liquid bleach	-	-	4.4	4.4
Powder bleach	-	-	0.68	0.7
Liquid fabric softener	2.1	2.2	-	2.2

[a]Source: Personal communication, Lever Brothers. Market volume for the period August 1988-July 1989. Average of 1988 and 1989 populations used to estimate per capita use.

[b]Source: Personal communication, The Procter & Gamble Company. 1988 market volume.

[c]Source: Personal communication, Clorox. 1988 market volume.

[d]Based on total U.S. population extrapolated using data from Statistical Abstracts, 1987. - 1988: 247×10^6; 1989: 249×10^6.

The per capita heavy metals contribution due to household cleaning product use was calculated as follows:

(i) The duplicate heavy metals analyses shown in Table 5 were averaged for each product category (Table 8).

(ii) Where the heavy metal content of a product category was less than the analytical detection limit, it was assumed that the product category contained the heavy metal at a concentration equal to the detection limit concentration (Table 8). This approach tended to overestimate the Cd, Cr_T, Cu, Pb, Hg, Ni, Ag, and Zn contributions of these household cleaning product categories.

(iii) The household cleaning product category heavy metals concentrations derived as above (Table 8) were multiplied by the USA per capita product category consumption (Table 7). The average of all 1988 and 1989 data presented in Table 7 was used.

The daily per capita heavy metals contributions from cleaning product useage is presented in Table 9.

The commonly cited reference for the heavy metals contributions of household cleaning products to wastewater is Gurnham et al. (1979). As indicated in Table 10, the Gurnham et al. values for the nickel concentration in powder and liquid laundry detergents is almost two orders of magnitude higher than other values reported in the literature, and almost three orders of magnitude higher than the nickel content of these products determined in the current study. Moreover, the Gurnham et al. values for some other heavy metals concentrations (e.g. copper and chromium) in powder and liquid laundry detergents appear to be high.

TABLE 8

AVERAGE HEAVY METALS CONCENTRATIONS IN CLEANING PRODUCT CATEGORIES, USED FOR CALCULATION OF HEAVY METALS CONTRIBUTIONS

Product Category	Average Heavy Metal Concentration in Product Category, mg/kg								
	As	Cd	Cr_T	Cu	Pb	Hg	Ni	Ag	Zn
Powder Laundry Detergent	13.8	0.26	1	0.49	0.2	0.025	0.5	0.5	7.27
Liquid Laundry Detergent	0.023	0.2	1	0.21	0.2	0.025	0.5	0.5	1.16
Liquid Bleach	0.005	0.2	1	0.2	0.2	0.025	0.5	0.5	2.89
Powder Bleach	20	0.72	1	0.3	0.2	0.025	0.5	0.5	5.01
Liquid Fabric Softener	0.011	0.2	1	0.2	0.2	0.025	0.5	0.5	0.5
Liquid Hand Dishwashing Detergent	0.013	0.2	1	0.2	0.2	0.025	0.5	0.5	0.5
Liquid Automatic Dishwashing Detergent	6.63	0.37	1	0.54	0.37	0.025	0.5	0.5	7.84
Powder Automatic Dishwashing Detergent	18.8	1.06	1	2.4	0.2	0.025	0.5	0.5	9.2

TABLE 9

DAILY PER CAPITA HEAVY METALS CONTRIBUTION FROM CLEANING PRODUCT USE

Product Category	Product Consumptions kg/capita/yr	Estimated Heavy Metal Contribution, mg/cap/day								
		As	Cd	Cr_T	Cu	Pb	Hg	Ni	Ag	Zn
Powder Laundry Detergent	6.1	0.23	0.0043	0.017	0.0082	0.0033	0.00042	0.0084	0.0084	0.12
Liquid Laundry Detergent	4.3	0.00027	0.0024	0.012	0.0025	0.0024	0.00029	0.0059	0.0059	0.014
Liquid Bleach	4.4	0.00006	0.0024	0.012	0.0024	0.0024	0.0003	0.006	0.006	0.035
Powder Bleach	0.7	0.037	0.0013	0.0019	0.00056	0.00037	0.00005	0.0009	0.00093	0.0093
Liquid Fabric Softener	2.2	0.00007	0.0012	0.006	0.0012	0.0012	0.00015	0.003	0.003	0.003
Liquid Hand Dishwashing Detergent	2.4	0.00009	0.0013	0.0066	0.0013	0.0013	0.00016	0.0033	0.0033	0.0033
Liquid Automatic Dishwashing Detergent	0.4	0.0073	0.00041	0.0011	0.00059	0.00041	0.00003	0.00055	0.0055	0.0086
Powder Automatic Dishwashing Detergent	1.0	0.052	0.0029	0.0027	0.0066	0.00055	0.00007	0.0014	0.0014	0.025
Product Total		0.33	0.016	0.059	0.023	0.012	0.0015	0.029	0.029	0.22

TABLE 10

COMPARISON OF CURRENT DATA ON HEAVY METALS CONCENTRATIONS IN POWDER AND LIQUID LAUNDRY DETERGENTS (THIS STUDY) WITH PREVIOUS DATA

	Average data for powder and liquid laundry detergents. Concentrations in mg/kg		
Metal	Average of previous data excluding Gurnham et al. (1979)[a]	Gurnham et al. (1979)	This study[c]
Cd	0.55[b]	0.85	0.23
Cr_T	1.9	6.7	1.0
Cu	2.6[b]	7.3	0.35
Pb	0.01[b]	1.0	0.2
Ni	4.6	300	0.5
Hg	-	0.01	0.025
Zn	83[b]	4.6	4.2

[a]Averages of ranges of data from Table 3 with no weighting for proportion of liquid and powder products analyzed. Data below detection limit taken as equal to the stated detection limit.

[b]One set of data only.

[c]From Table 8.

The data in Table 9, together with data from the reports by CH2M Hill, Inc., James M. Montgomery, Inc. and Eisenberg, Olivieri and Associates, Inc. for the three wastewater treatment plants can be used to calculate the contributions of heavy metals from various sources (i.e. household cleaning products, water supply, permitted industry and net residential) to the influent wastewaters. This data is presented, together with effluent heavy metals loads and current and future permit levels in Tables 11, 12, and 13 for the individual wastewater treatment plants. Table 14 presents a flow weighted average of these data for the three wastewater treatment plants. The net residential heavy metals contributions compared quite well with the average of the data from previous studies (Table 2) with the exception of mercury where data for only one study existed (much lower than previous data) and zinc (much higher than previous data). In Table 15 the heavy metals contributions of some of the sources in the influent wastewater to the total influent heavy metals loads are presented on a percentage basis.

The percentage contributions for some of the heavy metals do not add up to 100 percent because of (i) sources such as commercial and non-permitted industry were not included, (ii) the use of the average of "zero" and "detection limit value" for heavy metals reported as being below the detection limit, (iii) the use of data from only one or two of the treatment plants for some heavy metals, and (iv) general innaccuracies in conducting a mass balance on a complex and variable system.

Table 15 shows that for none of the heavy metals examined does the household cleaning products category contribute the highest percentage to the influent wastewater total heavy metals load. Only for arsenic (13 percent) is the contribution to the influent total heavy metals load above 1 percent. Also shown in Table 15 is the heavy metals contribution expressed as a percentage of the influent minus permitted industry heavy metals load. The data used for calculating this were obtained from the flow weighted average influent minus permitted industry heavy metals load from Table 14. On this basis the only household cleaning product heavy metal contribution above 1 percent is arsenic, at 16 percent.

It is appropriate to view the heavy metals content of wastewaters and their sources in wastewaters in terms of the current and proposed discharge permit limits. To do this realistically, one must examine the heavy metal contents of the wastewater treatment plant effluents rather than the influents. Two assumptions were made in developing this type of assessment:

(i) the future heavy metals removals achieved by the three treatment plants will be the same as the current values, and

(ii) the heavy metals from all sources in the influent wastewater are removed equally by the wastewater treatment plants.

TABLE 11

HEAVY METALS LOADS TO SAN JOSE/SANTA CLARA INFLUENT WASTEWATER AND FINAL EFFLUENT

Metal	Household Cleaning Products,[a] mg/cap/day	Water Supply,[b] mg/cap/day	Permitted Industry,[c] mg/cap/day	Net Residential,[d] mg/cap/day	Influent Wastewater,[e] mg/cap/day	Effluent: Current Actual Discharge, mg/cap/day	Effluent: Current Permit Level,[f] mg/cap/day	Effluent: Proposed Permit Level,[g] mg/cap/day[h]
As	0.33	1.3	0.64	0.49	2.9	1.7	3.8	7.6
Cd	0.016	1.2	0.41	0.2	3.7	0.95	7.6	3.8
Cr_T	0.059	3.5	2.4	--	23	1.4	3.8[i]	4.2[i]
Cu	0.023	8.7	11	11	91	4.3	76	7.6
Pb	0.012	0.75	5.3	1.9	27	3.6	38	2.1
Hg	0.0015	0.30	--	0.14	0.52	0.1	0.4	0.4
Ni	0.029	1.8	6.6	0.48	28	11	38	2.7
Ag	0.029	1.1	0.73	3.9	5.7	0.7	7.6	0.87
Zn	0.22	150	0.82	140	220	22	110	22

[a]From Table 9 of this report.
[b]Calculated from Table 4-5 CH2M Hill, Inc. (1989). Value is mean of range given in Table 4-5 which assumed that heavy metals analyzed as "non-detectable" are either "zero" or at the detection limit.
[c]Calculated from Table 5-9 CH2M Hill, Inc. (1989) on same basis as b above.
[d]Calculated from Tables 4-5 and 6-10 CH2M Hill, Inc. (1989) on same basis as b above.
[e]Calculated from Table 3-2 CH2M Hill, Inc. (1989).
[f]Interim limits; monthly averages; NPDES permit in effect until December, 1991.
[g]San Francisco Bay Basin Plan Table 4-1 (1986); daily averages; proposed effluent limitations to become effective in December, 1991.
[h]Assumes total wastewater flow of 100 gal/cap/day.
[i]Hexavalent Cr.

TABLE 12

HEAVY METALS LOADS TO PALO ALTO INFLUENT WASTEWATER AND FINAL EFFLUENT

						Effluent		
Metal	Household Cleaning Products,[a] mg/cap/day	Water Supply,[b] mg/cap/day	Permitted Industry,[c] mg/cap/day	Net Residential,[d] mg/cap/day	Influent Wastewater,[e] mg/cap/day	Current Actual Discharge,[j] mg/cap/day	Current Permit Level,[f] mg/cap/day	Proposed Permit Level,[g] mg/cap/day[h]
As	0.33	1.4	0.54	0.28	1.8	1.3	3.8	7.6
Cd	0.016	0.44	0.19	0.28	2.4	1.9	7.6	3.8
Cr_T	0.059	0.44	3.3	0.56	9.5	2.6	3.8[i]	4.2[i]
Cu	0.023	2.2	19	12	55	8.7	76	7.6
Pb	0.012	0.44	4.4	1.7	13	3.6	38	2.1
Hg	0.0015	0.91	0.05	--	0.19	0.12	0.4	0.4
Ni	0.029	1.4	5.9	0.56	7.7	4.5	38	2.7
Ag	0.029	0.44	5.2	3.0	11	1.3	7.6	0.87
Zn	0.22	32	8.0	24	92	31	110	22

[a]From Table 9 of this report.
[b]Calculated from Table 7-6, J. M. Montgomery Engineers (1989).
[c]Calculated from Table 7-8, J. M. Montgomery Engineers (1989).
[d]Calculated from Tables 7-6 and 7-7, J. M. Montgomery Engineers (1989).
[e]Calculated from Table 7-4, J. M. Montgomery Engineers (1989).
[f]Interim limits; monthly averages; NPDES permit in effect until December, 1991.
[g]San Francisco Bay Basin Plan Table 4-1 (1986); daily averages; proposed effluent limitations to become effective in December, 1991.
[h]Assumes total wastewater flow of 100 gal/cap/day.
[i]Hexavalent Cr.
[j]Calculated from Appendix E-1. J. M. Montgomery Engineers (1989). Assumes data reported as "less than" to be present at the value indicated as "less than." Assumes sewage flow of 100 gal/cap/day.

TABLE 13

HEAVY METALS LOADS TO SUNNYVALE INFLUENT WASTEWATER AND FINAL EFFLUENT

Metal	Household Cleaning Products,[a] mg/cap/day	Water Supply,[b] mg/cap/day	Permitted Industry,[c] mg/cap/day	Net Residential,[d] mg/cap/day	Influent Wastewater,[e] mg/cap/day	Effluent: Current Actual Discharge, mg/cap/day	Effluent: Current Permit Level,[f] mg/cap/day	Effluent: Proposed Permit Level,[g] mg/cap/day[h]
As	0.33	0.83	0.033	0.43	2.2	0.83	3.8	7.6
Cd	0.016	0.83	0.53	0.095	2.4	1.0	7.6	3.8
Cr_T	0.059	3.3	2.1	--	8.4	2.5	3.8[i]	4.2[i]
Cu	0.023	3.4	8.8	10	59	16	76	7.6
Pb	0.012	0.45	2.8	1.4	6.1	3.9	38	2.1
Hg	0.0015	0.60	--	--	0.73	0.3	0.4	0.4
Ni	0.029	1.8	4.1	0.19	--	6.3	38	2.7
Ag	0.029	0.45	0.83	2.6	3.2	4.8	7.6	0.87
Zn	0.22	170	--	12	190	--	110	22

[a] From Table 9 of this report.
[b] Calculated from Table 29, Eisenberg, Olivieri and Associates, Inc. (1989).
[c] Calculated from Table 21, Eisenberg, Olivieri and Associates, Inc. (1989).
[d] Calculated from Table 24, Eisenberg, Olivieri and Associates, Inc. (1989).
[e] Calculated from Table 11, Eisenberg, Olivieri and Associates, Inc. (1989).
[f] Interim limits; monthly averages; NPDES permit in effect until December, 1991.
[g] San Francisco Bay Basin Plan Table 4-1 (1986); daily averages; proposed effluent limitations to become effective in December, 1991.
[h] Assumes total wastewater flow of 100 gal/cap/day.
[i] Hexavalent Cr.

TABLE 14

AVERAGE[a] HEAVY METALS LOADS TO SOUTH SAN FRANCISCO BAY INFLUENT WASTEWATERS AND FINAL EFFLUENTS

Metal	Household Cleaning Products,[b] mg/cap/day	Water Supply, mg/cap/day	Permitted Industry, mg/cap/day	Net Residential, mg/cap/day	Influent Wastewater, mg/cap/day	Effluent: Current Actual Discharge, mg/cap/day	Effluent: Current Permit Level,[c] mg/cap/day	Effluent: Proposed Permit Level,[d] mg/cap/day[e]
As	0.33	1.2	0.55	0.45	2.6	1.6	3.8	7.6
Cd	0.016	1.1	0.39	0.21	3.3	1.1	7.6	3.8
Cr_T	0.059	3.0	2.5	0.56[g]	19	1.7	3.8[h]	4.2[h]
Cu	0.023	7.1	12	11	83	6.2	76	7.6
Pb	0.012	0.67	4.9	1.8	23	3.6	38	2.1
Hg	0.0015	0.43	0.05[g]	0.14[i]	0.49	0.12	0.4	0.4
Ni	0.029	1.7	6.2	0.47	24[f]	9.4	38	2.7
Ag	0.029	0.92	1.5	3.6	6.3	1.2	7.6	0.87
Zn	0.22	130	2.2[f]	110	200	23[f]	110	22

[a]Calculated from Tables 11, 12, and 13 of this report using a weighting factor proportional to tributary population as follows: San Jose/Santa Clara, 875,000; Palo Alto, 194,000; Sunnyvale, 120,000.
[b]From Table 9 of this report.
[c]Interim limits; monthly averages; NPDES permit in effect until December, 1991.
[d]San Francisco Bay Basin Plan Table 4-1 (1986); daily averages; proposed effluent limitations to become effective in December, 1991.
[e]Assumes total wastewater flow of 100 gal/cap/day.
[f]Data for San Jose and Palo Alto only.
[g]Data for Palo Alto only.
[h]Hexavalent Cr.
[i]Data for San Jose only.

TABLE 15

PERCENT CONTRIBUTIONS OF VARIOUS SOURCE CATEGORIES TO AVERAGE[a] INFLUENT HEAVY METALS LOADS TO SOUTH SAN FRANCISCO BAY WASTEWATER TREATMENT PLANTS (mg/cap/day)[b]

Metal	Household Cleaning Products,[g] %		Other Net Residential Sources, %	Water Supply, %	Permitted Industry, %
As	13	(16)	5	46	21
Cd	0.5	(0.5)	6	33	12
Cr_T	0.3	(0.3)	1[d]	16	12
Cu[c]	0.03	(0.03)	13	9	14
Pb[c]	0.05	(0.07)	8	3	21
Hg	0.3	(0.3)	27[f]	88	26[d]
Ni[c,e]	0.1	(0.2)	2	7	24
Ag[c]	0.5	(0.6)	57	15	22
Zn[c]	0.1	(0.1)	55	65	1

[a]Calculated from Tables 11, 12, and 13 of this report using a weighting factor proportional to tributary population as follows: San Jose/Santa Clara, 875,000; Palo Alto, 194,000; Sunnyvale, 120,000.
[b]Calculated from data in Table 14.
[c]Future permit level exceeded by current effluent heavy metals loadings.
[d]Based on Palo Alto data only.
[e]All nickel contributions based on San Jose and Palo Alto influents only.
[f]Based on San Jose data only.
[g]Numbers in ( ) are percent contributions to influent minus permitted industry.

The current flow weighted average heavy metals removals for the three wastewater treatment plants are presented in Table 16. In Table 17 the current effluent heavy metals discharge levels are compared to the current and proposed permit limits both for the flow weighted average values of the three wastewater treatment plants and for the individual treatment plants. In Table 17, numbers in bold print indicate that the current effluent heavy metal discharge is 80 percent or more of the proposed discharge permit level. For the flow-weighted average effluent data, copper, lead, nickel, silver and zinc are in excess of the proposed discharge permit levels. None of the flow weighted average effluent heavy metals exceed 50 percent of the current discharge permit levels.

Using the percentage heavy metals removals by wastewater treatment, the contributions of various sources of heavy metals to the influent wastewater and the current and proposed permit limits, the contributions from the various heavy metals sources can be expressed as a percentage of the current and propoesd permit limits. This is done for the current permit limits in Table 18 and for the proposed permit limits in Table 19.

Based on this data household cleaning products were never the greatest source of heavy metals of the contributions listed (i.e. household cleaning products, other net residential, water supply and permitted industry). Only for arsenic is the household cleaning product contribution in excess of 1 percent of either the current or the proposed discharge permit limits. Household cleaning products contribute 5 percent of the arsenic to the current discharge limit, and 3 percent of the arsenic to the proposed discharge limits. It should also be noted that the current effluent arsenic level is well below both the current and proposed discharge limits. Tables 20-23 summarize the average flow weighted heavy metals data in terms of the contributions of individual sources to the net residential heavy metals load, the current wastewater influent and effluent heavy metals loads and the current and proposed heavy metals discharge limits. Table 20 shows that the household cleaning product contribution to the net residential heavy metals load is 73 percent for arsenic, 11 percent for chromium, 8 percent for cadmium, 6.2 percent for nickel and 1.1 percent for mercury. For silver, lead, copper and zinc the contribution is less than 1 percent. Even though household cleaning products contribute the majority of the arsenic to net residential wastewater, this results in a minor (13 percent) contribution to the influent and effluent wastewater and an even smaller contribution (5 percent and 3 percent, respectively) to the current and proposed discharge permit levels.

TABLE 16

AVERAGE[a] HEAVY METALS REMOVALS BY
SOUTH SAN FRANCISCO BAY WASTEWATER TREATMENT PLANTS

Metal	Influent[b] Wastewater, mg/cap/day	Current Effluent Wastewater, mg/cap/day	Removal %
As	2.6	1.6	38
Cd	3.3	1.1	67
Cr_T	19	1.7	91
Cu	83	6.2	93
Pb	23	3.6	84
Hg	0.49	0.12	76
Ni	24[c]	9.8[c]	59
Ag	6.3	1.2	81
Zn	196[c]	23[c]	88

[a]Calculated from Tables 11, 12, and 13 of this report using a weighting factor proportional to tributary population as follows: San Jose/Santa Clara, 875,000; Palo Alto, 194,000; Sunnyvale, 120,00.
[b]Data from Table 14 of this report.
[c]Data based on San Jose and Palo Alto only.

TABLE 17

AVERAGE[a] AND INDIVIDUAL EFFLUENT HEAVY METALS LOADS FOR SOUTH SAN FRANCISCO BAY WASTEWATER TREATMENT PLANTS EXPRESSED AS A PERCENTAGE OF CURRENT AND PROPOSED PERMIT LIMITS

Metal	Current Average Effluent Discharge as % of:		Individual Plant Current Effluent Discharge as % of Proposed Permit Limits		
	Current Permit Limit	Proposed Permit Limit	San Jose/ Santa Clara	Palo Alto	Sunnyvale
As	42	21	22	17	11
Cd	14	29	25	50	26
Cr_T[b]	45	40	33	62	60
Cu	8	**82**[c]	57	**110**	**210**
Pb	9	**170**	**170**	**170**	**190**
Hg	30	30	25	30	75
Ni	25	**350**	**410**	**170**	**230**
Ag	16	**140**	**80**	**150**	**550**
Zn	21[d]	**105**	**100**	**140**	-

[a]Calculated from Tables 11, 12, and 13 of this report using a weighting factor proportional to tributary population as follows: San Jose/Santa Clara, 875,000; Palo Alto, 194,000; Sunnyvale, 120,000.
[b]Cr limit is for hexavalent Cr.
[c]Bold face numbers indicate effluent discharge values that are > 80 percent of indicated permit limit.
[d]Data for San Jose and Palo Alto only.

TABLE 18

AVERAGE PERCENT EFFLUENT HEAVY METALS CONTRIBUTIONS[a] TO CURRENT PERMIT LEVELS, SOUTH SAN FRANCISCO BAY

	Percent Contribution From:			
Metal	Household Cleaning Products[g]	Other Net Residential Sources	Water Supply	Permitted Industry
As	5	2	19	9
Cd	0.07	0.8	5	2
Cr_T[b]	0.1	0.1[c]	7	6
Cu	0.002	1	0.7	1
Pb	0.005	0.8	0.3	2
Hg	0.09	8[d]	25	3[c]
Ni	0.03	0.5	2	7
Ag	0.07	9	2	4
Zn	0.02	12	15	0.2[e]

[a]Assumes average influent heavy metals loads are removed by amounts indicated in Table 16.
[b]Permit is for hexavalent Cr.
[c]Data for Palo Alto only.
[d]Data for San Jose only.
[e]Data for San Jose and Palo Alto only.

TABLE 19

AVERAGE PERCENT EFFLUENT HEAVY METALS CONTRIBUTIONS[a] TO FUTURE PERMIT LEVELS, SOUTH SAN FRANCISCO BAY

	Percent Contribution from:			
Metal	Household Cleaning Products[g]	Other Net Residential Sources	Water Supply	Permitted Industry
As	3	1	10	5
Cd	0.1	2	9	3
Cr_T[c]	0.1	0.1[d]	6	5
Cu[b]	0.02	10	7	10
Pb[b]	0.09	14	5	37
Hg	0.09	8[e]	25	3[d]
Ni[b]	0.4	7	26	93
Ag[b]	0.6	78	20	32
Zn[b]	0.1	59	73	1[f]

[a]Assumes average influent heavy metals loads are removed by amounts indicated in Table 16.
[b]At current heavy metals loadings and removals permit will be exceeded.
[c]Data for Palo Alto only.
[d]Data for San Jose only.
[e]Data for San Jose and Palo Alto only.

TABLE 20

AVERAGE PERCENT HEAVY METALS CONTRIBUTION[a] OF HOUSEHOLD CLEANING PRODUCTS TO NET RESIDENTIAL WASTE, CURRENT INFLUENT AND EFFLUENT LOADS, AND CURRENT AND FUTURE PERMIT LEVELS FOR SOUTH SAN FRANCISCO BAY

Metal	Percent Contribution of Household Cleaning Products to Heavy Metals in:			
	Net Residential Load	Current Influent and Effluent Loads	Current Permit Level	Future Permit Level
As	73	13	5	3
Cd	8	0.5	0.07	0.1
Cr_T	11[d]	0.3	0.1[c]	0.1[c]
Cu[b]	0.2	0.03	0.002	0.02
Pb[b]	0.7	0.05	0.005	0.09
Hg	1.1[e]	0.3	0.09	0.09
Ni[b]	6.2	0.1	0.03	0.4
Ag[b]	0.8	0.5	0.07	0.6
Zn[b]	0.2	0.1	0.02	0.1

[a]Assumes average influent heavy metals loads are removed by amounts indicated in Table 16.
[b]At current heavy metals loadings and removals permit will be exceeded.
[c]Permit is for hexavalent Cr.
[d]Data for Palo Alto only.
[e]Data for San Jose only.
[f]Data for San Jose and Palo Alto only.

TABLE 21

AVERAGE PERCENT HEAVY METALS CONTRIBUTION[a] OF NET RESIDENTIAL SOURCES OTHER THAN HOUSEHOLD CLEANING PRODUCTS TO NET RESIDENTIAL WASTE, CURRENT INFLUENT AND EFFLUENT LOADS, AND CURRENT AND FUTURE PERMIT LEVELS FOR SOUTH SAN FRANCISCO BAY

Metal	Percent Contribution of Net Residential Sources Other Than Household Cleaning Products to Heavy Metals in:			
	Net Residential Load	Current Influent and Effluent Loads	Current Permit Level	Future Permit Level
As	27	5	2	1
Cd	92	6	0.8	2
Cr_T	89	3	0.1[c]	0.1[c]
Cu[b]	>99	13	1	10
Pb[b]	>99	8	0.8	14
Hg	99[d]	28[d]	8[d]	8[d]
Ni[b]	94	2	0.5	7
Ag[b]	>99	57	9	78
Zn[b]	>99	55	12	59

[a]Assumes average influent heavy metals loads are removed by amounts indicated in Table 16.
[b]At current heavy metals loadings and removals permit will be exceeded.
[c]Permit is for hexavalent Cr.
[d]Data for San Jose only.

TABLE 22

AVERAGE PERCENT HEAVY METALS CONTRIBUTION[a] OF WATER SUPPLY TO CURRENT INFLUENT AND EFFLUENT LOADS, AND CURRENT AND FUTURE PERMIT LEVELS FOR SOUTH SAN FRANCISCO BAY

Metal	Percent Contribution of Water Supply to Heavy Metals in:		
	Current Influent and Effluent Loads	Current Permit Level	Future Permit Level
As	46	20	10
Cd	33	5	9
Cr_T	16	7[c]	6[c]
Cu[b]	9	0.7	7
Pb[b]	3	0.3	5
Hg	88	25	25
Ni[b]	7[d]	2	26
Ag[b]	15	2	20
Zn[b]	65	15	73

[a]Assumes average influent heavy metals loads are removed by amounts indicated in Table 16.
[b]At current heavy metals loadings and removals permit will be exceeded.
[c]Permit is for hexavalent Cr.
[d]Data for San Jose and Palo Alto only.

TABLE 23

AVERAGE PERCENT HEAVY METALS CONTRIBUTION[a] OF PERMITTED INDUSTRY TO CURRENT INFLUENT AND EFFLUENT LOADS, AND CURRENT AND FUTURE PERMIT LEVELS FOR SOUTH SAN FRANCISCO BAY

Metal	Percent Contribution of Permitted Industry to Heavy Metals in:		
	Current Influent and Effluent Loads	Current Permit Level	Future Permit Level
As	21	9	5
Cd	12	2	3
Cr_T	13	6[c]	5[c]
Cu[b]	14	1	11
Pb[b]	21	2	37[d]
Hg	10[d]	3[d]	3[d]
Ni[b]	26[e]	7	93
Ag[b]	24	4	32
Zn[b]	1[e]	0.2[e]	1[e]

[a]Assumes average influent heavy metals loads are removed by amounts indicated in Table 16.
[b]At current heavy metals loadings and removals permit will be exceeded.
[c]Permit is for hexavalent Cr.
[d]Data for Palo Alto only
[e]Data for San Jose and Palo Alto only.

Summary and Conclusions

A study that involved the sampling and analysis for heavy metals of influent and effluent wastewaters, domestic water supplies, industrial, commercial and residential discharges and household cleaning products was conducted in the Southern San Francisco Bay area. A population base of some 1.2 million people was involved. The household cleaning products included laundry and dishwashing detergents, bleaches and fabric softeners. The flow-weighted average heavy metals contributions of household cleaning products, other net residential sources, water supply and permitted industry to the influent and effluent wastewater and to current and proposed discharge permit levels were determined. For none of the heavy metals examined did household cleaning products contribute the highest percentage to the influent wastewater total heavy metals. Only for arsenic (13 percent) was the contribution above 1 percent. In terms of their contributions to current and proposed heavy metals discharge permit levels, household cleaning products were never the major heavy metals source for the heavy metals examined. Household cleaning products contributed 5 percent of the arsenic load to the current NPDES discharge permit level and 3 percent to the proposed NPDES discharge permit levels. The current effluent arsenic content is well below both the current and proposed discharge limit. For all other heavy metals the contribution was less than 1 percent. When expressed in terms of their contributions to the net residential wastewater only, household cleaning products contributed 73 percent of the arsenic, 11 percent of the chromium, 8 percent of the cadmium, 6.2 percent of the nickel and 1.1 percent of the mercury. For silver, lead, copper and zinc, household cleaning products contributed less than 1 percent to the net residential wastewater component.

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APPENDIX 1

CLEANING PRODUCT USAGE DATA

AND COMPOSITING PROCEDURES

(Source: Hazelton Laboratories America, Inc. (1990))

TABLE 24

MARKET SHARE AND TARGET COMPOSITE SAMPLE WEIGHTING FACTORS FOR THE VARIOUS BRANDS OF VARIOUS HOUSEHOLD CLEANING PRODUCTS

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	DowBrands	2	63	3
Powder Bleach:				
Clorox II	Clorox	42	42	53
Biz	Procter & Gamble	27	69	34
Borateem	Dial	11	80	14

TABLE 24 (Continued)

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

TABLE 25

DESCRIPTION OF TARGET CLEANING PRODUCT COMPOSITING PROCEDURE

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

Powder Laundry Detergents (42 oz. size)

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

Note: No Purex or Dash was sent from Palo Alto. Sunnyvale sent Lemon Fresh Dash; San Jose sent Regular Dash.

Liquid Laundry Detergents (62 fluid oz. size)

Liquid Tide	500 g	25%
Wisk	480 g	24%
Liquid All	340 g	17%
Liquid Cheer	140 g	7%
Era	140 g	7%
Liquid Surf	140 g	7%
Liquid Bold	120 g	6%
Liquid Arm and Hammer	120 g	6%
	1,980 g	99%

Liquid Bleaches (128 fluid oz. size)

Clorox	1,420 g	71%
Purex	340 g	17%
Clorox II	160 g	8%
Vivid	60 g	3%
	1,980 g	99%

Note: No Vivid was sent from Palo Alto.

Powder Bleaches (32 oz. size)

Clorox II	1,060 g	53%
Biz	680 g	34%
Borateem	280 g	14%
	2,020 g	101%

Liquid Fabric Softeners (22 fluid oz. size)

Downy (Regular)	1,080 g	54%
Snuggle	560 g	28%
Downy (Sun Rinse)	360 g	18%
	2,000 g	100%

Liquid Hand Dishwashing Detergents (22 fluid oz. size)

Palmolive Liquid	380 g	19%
Dawn	300 g	15%
Ivory Liquid	280 g	14%
Crystal White Octagon	280 g	14%
Joy	280 g	14%
Sunlight	260 g	13%
Dove	200 g	10%
	1,980 g	99%

Note: No Ivory Liquid was sent from Palo Alto.

Liquid Automatic Dishwashing Detergents (32 fluid oz. size)

Cascade	740 g	37%
Palmolive Liquid	640 g	32%
Sunlight Liquid	600 g	30%
	1,980 g	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 was not used in the composite. Due to analyst error, only one fourth of the San Jose Sunlight Liquid was available for use in the composite.

Powder Automatic Dishwashing Detergents (50 oz. size)

Cascade	1,400 g	70%
Sunlight	360 g	18%
Electrosol	220 g	11%
	1,980 g	99%

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

From these data it can be concluded that the target compositing procedure was met satisfactorily.

APPENDIX 2

ANALYTICAL METHODS FOR HEAVY METALS IN COMPOSITE CLEANING PRODUCTS SAMPLES

(Hazelton Laboratories America, Inc. (1990))

I. MATERIALS

A. Reagents

1. Water, double deionized
2. Nitric acid, GR grade, EM Science, NX0409-7
3. Sulfuric acid, GR grade, EM Science, SX1244-5
4. Sodium borohydride, Fisher Scientific, S678-25
5. Stock solutions of metallic elements, 1,000 mg/l Fisher Scientific

B. Equipment

1. Atomic Absorption Spectrophotometer, Perkin-Elmer Model 5000
2. Mercury/hydride system, Perkin-Elmer MHS-20.

II. SAMPLE PREPARATION

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

1. The powder laundry detergents, liquid laundry detergents, powder bleaches, liquid automatic dishwashing detergents, and automatic dishwashing detergents were digested with nitric acid in beaker on a hot plate. After transfer to a 50 ml volumetric flask, the samples were filtered through Fisher coarse filter paper to remove particulates.

2. The liquid bleaches, liquid fabric softeners, and liquid hand dishwashing detergents were dry-ashed on hot plates.

3. All six elements were determined on the same digest.

B. Silver

1. The powder laundry detergents, liquid laundry detergents, powder bleaches, and liquid and powder automatic dishwashing detergents were digested with nitric acid in a beaker on a hot plate. The sample was filtered through Fisher coarse filter paper to remove particulates.

2. The liquid bleaches, liquid fabric softeners, and liquid hand dishwashing detergents were dry-ashed on hot plates.

3. After setting for several hours, the liquid bleach and liquid laundry detergent composites usually separated. The detergent was rehomogenized by shaking. The bleach was rehomogenized by processing with a Polytron.

4. The liquid bleach was accidentally contaminated with copper when it was processed on the Polytron in preparation for the mercury digestion. The bleach was recomposited on August 31, 1989, with the following weights:

Clorox	355 g	71%
Purex	85 g	17%
Clorox II	40 g	8%
Vivid	15 g	3%
	495 g	99%

C. Mercury

1. The samples were digested with a mixture of sulfuric and nitric acids. The mercury was reduced with sodium borohydride using the Perkin-Elmer MHS-20 Hydride System.

D. Arsenic

1. The samples were digested with a mixture of sulfuric and nitric acids. The arsenic was converted to arsine using the Perkin-Elmer MHS-20 Hydride System.

III. PREPARATION OF SAMPLE SPIKES

A. For all analytes, the samples were spiked and digested as described above. The choice of spiking level 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 four times the detection limit. For samples with quantifiable analyte levels, spikes were added at five times the levels found.

IV. METHOD REFERENCES

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B. Arsenic

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H. Nickel

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