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PRIORITY POLLUTANTS IN MUNICIPAL WASTEWATERS

Municipal wastewater is a complex mixture of substances, many of which are toxic at some level. Some of these sub-stances have not been chemically identified, nor have their thresholds of toxicity in the marine environment been determined. As a step in correcting this situation, the U.S. Environmental Protection Agency (EPA) established a list of "Priority Pollutants,"--approximately 120 trace organics, 15 metallic constituents, and 15 conventional wastewater parameters--and specified that primary-treated wastewaters discharged to marine waters be analyzed for these substances (Federal Register 1978a). In the past year, the Coastal Water Research Project has coordinated the efforts of southern California's major dischargers to assemble the required data. The results of this program are presented here; we have also included data on secondary wastewaters and sludges and centrates, wherever possible.

One of the principal findings of the study was that, on the average, less than 10 percent of the target trace organics were found to be present at levels above the mandated quantification limit of 10 micrograms/liter or parts per billion (ppb) in the various wastewaters analyzed. Although concentrations of a number of volatile constituents appeared to be substantially reduced by secondary treatment, the evidence suggests that the majority of these reductions are the result of losses to the atmosphere. In addition, second-ary treatment produced only modest reductions in the levels of most trace metals. However, there were major reductions in the concentrations of asbestos and certain conventional parameters with secondary treatment.

PROCEDURES

During the summer of 1978, replicate 24-hour flow-proportioned composite samples of primary- and secondary-treated wastewaters, sludges, and centrates were collected from the four largest publicly owned treatment plants in southern California. Samples were collected from the Hyperion Treatment Plant of Los Angeles City on 20-21 July, from the Point Loma Treatment Plant of San Diego City on 24-25 July, from Orange County Sanitation Districts' treatment plant on 27-28 July, and from the Joint Water Pollution Control Plant (JWPCP) of Los Angeles County Sanitation Districts on 28 July. The JWPCP effluent samples were obtained by plant personnel with the help of automatic samplers; the composite samples from the other three plants, which do not have automatic samplers, were collected hourly by Project personnel in cleaned metal or plastic buckets (depending on the target analysis). Additional grab samples were obtained and pre-served separately for analyses for certain constituents. For example, the procedures specified by the EPA (U.S. Environmental Protection Agency 1977; Federal

Register 1978b) required that samples for volatile organic analyses be immediately transferred after collection to special air-tight vials without introduction of any visible bubbles.

On the order of 3,000 chemical determinations were made in the course of the investigation. A list of the target trace organics is given in Table 1; the metallic and conventional parameters (the latter broken into two categories--general and miscellaneous) are listed in Table 2. A number of laboratories were involved in the analyses. Asbestos levels in Point Loma, Hyperion, and Orange County samples were determined by Ontario Research Foundation (Ontario, Canada); Carborundum Company (Niagara Falls, N.Y.) and California Analytic Laboratories (Sacramento) analyzed these effluents for trace metals and organics; and the individual plant laboratories performed tests for the conventional parameters. The gas chromatography/mass spectrometry (GC/MS) analysis of most volatile and extractable organics in the JWPCP samples was conducted by Montgomery Engineers (Pasadena, Calif.) and Analytic Research Laboratories (Monrovia, Calif.); the other parameters were measured at the Los Angeles County Sanitation Districts' laboratories.

The procedures specified by EPA included the analysis of one of the two samples immediately after mixing and the analysis of the supernatant of the other sample after 3 hours of quiescent settling. Any chlorinated pesticide values above 1 ppb were to be reported; the quantification limit for the other trace organics was 10 ppb.

RESULTS

Values obtained for the Los Angeles County wastewaters are listed in Table 2; those for the other dischargers are given in Table 3. Values have been corrected, wherever possible, for procedural blanks. Each table has been shortened by deleting any target trace organic (Table 1) that was not quantified in at least one effluent considered in that table.

Several irregularities and data reduction procedures should be noted:

1. Concentrations of most of the conventional parameters and many of the metals on the EPA list are routinely monitored by the discharging agencies. In some cases (noted in footnotes to Tables 2 and 3), monitoring data for 1977 and 1978 are reported here, rather than the results of the analysis of the summer 1978 samples, because the former are based on a greater number of analyses and thus are presumably more reliable.

2. As many of the target substances are associated with wastewater particulates, the value of the prescribed analysis of a wastewater sample drawn after particulates had been allowed to settle seemed questionable, particularly in view of the fact that the effluents under consideration are discharged to the ocean, where flocculation caused by mixing with the saline waters can result in deposition of effluent particulates. Therefore, whenever the values from the analysis of mixed and supernatant samples seemed relatively precise, we have listed only the result of the analysis of the mixed sample: Any result given for the general and metallic constituents that was not taken from monitoring data is from the mixed sample analysis.

Measurements of the target organics and miscellaneous constituents were much less certain, and comparison of the results from the mixed and settled samples revealed no general trend (i.e., the former values were not systematically higher than the latter).

Therefore, the two values obtained for each of these constituents were averaged to increase the statistical base. In those cases where there was only one value above the GC/MS quantification limit of 10 ppb, the other value was assumed to be 5 ± 5 ppb to obtain estimated average and standard error values; the un-certainty added to the resultant average cannot exceed 2.5 ppb. (The data for the Los Angeles County wastewaters included some estimated concentrations below 10 ppb; when only one of these estimates was obtained, it is listed alone.)

On the average, the relative standard error between values for the two samples was less than 50 percent. This appears to be satisfactory in view of the complexities involved in sample collection, preparation, and GC/MS analysis. In any event, the trace organic data (most of which are the first ever reported for these major wastewater treatment plants) do provide an order-of-magnitude estimate of a wastewater concentration of a substance, or a 10-ppb upper limit on the concentration, following various levels of treatment.

3. Orange County Sanitation Districts are presently considerably altering their treatment and discharge procedures, a process due to be completed by 1983. Therefore, in meeting EPA's requirements, this agency elected to combine the values from their analyses of their primary, secondary, and centrate wastewaters, proportionately weighting them to obtain estimates of the concentrations of the various constituents in the final effluent to be discharged when the treatment alterations are completed. For three sets of analyses not done in the treatment plant laboratories—those for extractable organics, miscellaneous constituents, and metals, the Districts created composite samples of their present wastewaters to simulate the "projected 1983 effluent."

One of the Project's goals in conducting the program described here was to examine each discharger's data on its various wastewaters and note the effects of advanced levels of treatment. Therefore, in completing Table 3, we used data on Orange County's individual wastewaters, wherever available, rather than any projected values. The values given for extractable organics, miscellaneous constituents, and certain of the metals are for the projected effluent, which is expected to total 3.13×10^{11} liters/year and to be 33 percent primary, 66 percent secondary, and 0.3 percent centrate effluent.

4. It should be noted that, during the time of sampling for this survey, the Point Loma Treatment Plant was operating somewhat below its usual efficiency. As a result, the final effluent analyzed in the survey contained considerably higher concentrations of the conventional waste-water parameters than normal. For example, the summer 1978 24-hour composites contained 29 percent more total suspended solids, 60 percent more oil and grease, and 36 percent more BOD than the effluent of this plant has contained, on the average, in recent years. The subnormal operating efficiency probably caused the values for many other parameters listed in Table 3 to be somewhat higher than is representative of normal operating conditions.

DISCUSSION

Relatively few of the target trace organics for this survey were found to be present at levels above the 10-ppb quantification limit. Although the Priority Pollutant list contains 120 of these compounds, less than 5 percent were quantified in the San Diego primary

(final) effluent, approximately 10 percent were quantified in the Orange County and the Los Angeles City primary effluents, and approximately 15 percent were found at levels exceeding 10 ppb in both the Los Angeles County primary and final effluents. As these wastewater effluents undergo an average initial dilution of at least 100 to 1 following submarine discharge, the results indicate that the concentrations of the large majority of the trace organics of concern in the seawater in the discharge zone are less than 0.1 ppb. Actual concentrations may well be much lower. In future investigations of this nature, the blanket 1- and 10-ppb quantification limits should be dropped, and the lowest detectable level of each compound should be reported, at least until there is more information on the bioaccumulation capabilities and thresh-olds of toxicity of these compounds.

The data also indicate that the secondary effluents of Los Angeles City, Los Angeles County, and Orange County generally contain much lower concentrations of trace organics than do the corresponding primary effluents. This is most evident in the case of the volatile organics (Table 1), suggesting that these contaminants may be carried away with the gases that are used to mix the effluents during the secondary treatment processes. The volatile organics were also found in relatively low concentrations in Los Angeles City's 7-mile sludge effluent (which is 25 percent digested primary and secondary sludge, 75 percent secondary effluent), as well as in Orange County's "centrate" (effluent from centrifuged primary sludge) .

Los Angeles County's data on volatile organics have one pattern that is very different from those of the other dischargers with advanced treatments: Although this discharger's secondary wastewater concentrations of many of the measurable volatile or extractable organics are an order of magnitude below the primary wastewater levels, the final effluent concentrations of most of these compounds exceed those of the primary wastewaters. The situation is somewhat obscured by the way this plant analyzed and reported its data. Unlike Los Angeles City and Orange County, which per-formed separate analyses of the components of their final effluents, Los Angeles County analyzed its primary and secondary wastewaters but did not separately analyze its centrate: Instead, a separate analysis was performed on the final JWPCP effluent, which is 0.7 percent centrate. The relatively high values for certain of the trace organic compounds for the final effluent, if not the result of a systematic bias in sampling or analysis, indicate that the centrate that was added to the primary and secondary waste-waters had remarkably high levels of these trace organics. Plainly, representative samples of JWPCP centrate should be analyzed directly for trace organic (and other) constituents of interest.

Additional information on certain trace organics has been obtained in this investigation. Los Angeles County Sanitation Districts arranged for GC/MS analysis of extract- able organics in tissues of intertidal mussels collected in December 1977 by Project personnel at Royal Palms Beach (at the base of JWPCP outfalls) and at an island control site (San Nicolas Island). Although 2,4-dimethylphenol, pentachlorophenol, and phenol were measurable in the JWPCP final effluent (5, 30, and 650 ppb, respectively), neither these nor the vast majority of the other 120 trace organics of concern were detected in the whole soft tissues of the out- fall (or control) mussels. The only synthetic organics measured were the higher molecular weight chlorinated hydro- carbons—total DDT, PCB 1242, and PCB 1254 (0.4, 0.01 and 0.05 mg/wet kg, respectively). The levels of these sub- stances are somewhat lower than those measured in Royal Palms

mussels in the past (Young and Heesen 1978), reflecting the gradual decline in the amounts of these contaminants in the Palos Verdes environment following the source and use control of DDT and PCB that was initiated in the early 1970's.

The trace metal data from the three dischargers with secondary treatment processes show a similar pattern: Metals concentrations in the secondary wastewaters, although often lower by a few factors, are generally of the same order as those in the primary wastewaters. The most notable exceptions are the chromium and copper concentrations in Los Angeles City and County wastewaters, which are apparently reduced as much as eight times by secondary treatment. In addition, secondary treatment appears to be an order of magnitude more effective than primary treatment in reducing the concentrations of asbestos and certain of the conventional wastewater constituents, such as suspended solids, biological and chemical oxygen demand, oil and grease, and fecal coliforms.

One final comment about the design of the survey should be made. We estimate that the total cost of collecting and analyzing one set of samples for the 150 constituents specified by the EPA is approximately $6,000. With this high cost in mind, we must question the EPA requirement that both a mixed and supernatant sample of each effluent be analyzed for each constituent. Although the second analysis may be of interest in surveys of wastewaters to be discharged to freshwater, the settling that a freshwater effluent under-goes is known to be much smaller than the settling that occurs when an effluent undergoes flocculation caused by dilution with a saline solution like seawater. Thus, the concentrations of trace contaminants on the particulates of a marine effluent are of great interest, and the value of the results from analysis of a sample of effluent not containing all these particulates is questionable. We recommend that, in any future surveys of this type, the requirement for analysis of the supernatant of marine effluents after 3 hours of settling be dropped.

REFERENCES

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Table 1. Trace organic substances on EPA's list of Priority Pollutants.

Acenaphthene
Acrolein*
Acrylonitrile*
Aldrin
Benzene*
Benzidine
Carbon tetrachloride*
Chlordane
Chlorobenzene*
1,2,3-trichlorobenzene
Hexachlorobenzene
Chloroethane*
1,1-dichloroethane*
1,2-dichloroethane*
1,1,1-trichloroethane*
1,1,2-trichloroethane*
1,1,2,2-tetrachloroethane*
Hexachloroethane
Bis (chloromethyl) ether
Bis (2-chloroethyl) ether
2-chloroethyl vinyl ether*
2-chloronaphthalene
2,4-dichlorophenol
2,4,6-trichlorophenol
Parachlorometacresol
Chloroform*
2-chlorophenol
4,4'-DDT
4,4'-DDE
4,4'-DDD
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
3,3'-dichlorobenzidine
1,1-dichloroethylene*
1,2-trans-dichloroethylene*
1,2-dichloropropane*
1,3-dichloropropene*
Dieldrin
2,4-dimethylphenol
2,4-dinitrotoluene
2,6-dinitrotoluene
1,2-diphenylhydrazine
α-endosulfan
β-endosulfan
Endosulfan sulfate
Endrin
Endrin aldehyde
Ethylbenzene*
Fluoranthene
4-chlorophenylphenyl ether
4-bromophenylphenyl ether
Bis (2-chloroisopropyl) ether
Bis (2-chloroethoxy) methane
Methylene chloride*
Methyl chloride*
Trichlorofluoromethane*
Dichlorodifluoromethane*
Methyl bromide*
Bromoform*
Dichlorobromomethane*
Chlorodibromomethane*
Heptachlor
Heptachlor epoxide
Hexachlorobutadiene
Hexachlorocyclopentadiene
α-hexachlorocyclohexane
β-hexachlorocyclohexane
γ-hexachlorocyclohexane
δ-hexachlorocyclohexane
Isophorone
Naphthalene
Nitrobenzene
2-nitrophenol
4-nitrophenol
2,4-dinitrophenol
4,6-dinitro-o-cresol
N-nitrosodimethylamine
N-nitrosodiphenylamine
N-nitrosodi-n-propylamine
Pentachlorophenol
Phenol
Bis (2-ethylhexyl) phthalate
Butylbenzyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Diethyl phthalate
Dimethyl phthalate
Pyrene
Benzo[a]pyrene
Benzo[e]fluoranthene
Benzo[j]fluoranthene
Benzo[k]fluoranthene
Benz[a]anthracene
Chrysene
Anthracene
Benzo[ghi]perylene
Fluorene
Phenanthrene
Dibenz[a,h]anthracene
Indeno[1,2,3-cd]pyrene
PCB 1242
PCB 1254
PCB 1221
PCB 1232
PCB 1248
PCB 1260
PCB 1016
2,3,7,8-tetrachlorodibenzo-p-dioxin
Tetrachloroethylene*
Toluene*
Toxaphene
Trichloroethylene*
Vinyl chloride*
Demeton**
Guthion**
Malathion**
Methoxychlor**
Mirex**
Parathion**

*Volatile organic; all others are extractable.
**Pesticide added to Priority Pollutant list after its original publication.

Table 2. Concentrations (mean ± standard error) of EPA Priority Pollutants in the Los Angeles County JWPCP effluents, based on analyses of 24-hour composite or grab samples collected in July 1978[a] (NA means "not analyzed").

	Primary	Secondary	Final[b]
Flow (liters/yr x 10^{11})	4.71	0.007	4.75
pH	7.3	7.3	7.6
General constituents (mg/liter)			
Total suspended solids	131	18	220
Oil and grease	34	1.6	46
Ammonia nitrogen	37	30	39
Nitrate nitrogen	NA	NA	<0.2
Total (K) nitrogen	49	NA	53
Total phosphorus	20	NA	23
BOD	200	9.0	220
COD	460	83	560
Fecal coliform (MPN/100 ml)	7.5×10^6	7.5×10^4	2.5×10^6
Volatile organics (µg/liter)			
Benzene	200 ± 34	22 ± 2	580 ± 43
Carbon tetrachloride	12 ± 2	16 ± 0	16 ± 2
Chlorobenzene	12 ± 7	3	8
1,2-dichloroethane	<10	11 ± 1	54 ± 2
1,1,1-trichloroethane	130 ± 15	180 ± 15	190 ± 5
Chloroform	34 ± 0	30 ± 2	46 ± 1
Ethylbenzene	130 ± 6	18 ± 4	220 ± 1
Methylene chloride	24 ± 2	4 ± 0	11 ± 4
Dichlordifluoromethane	6	<10	<10
Dichlorobromomethane	<10	6	<10
Tetrachlorcethylene	54 ± 14	160 ± 25	140 ± 4
Toluene	310 ± 24	24 ± 4	1,200 ± 60
Trichloroethylene	140 ± 5	12 ± 2	72 ± 4
Extractable organics (µg/liter)			
Acenaphthene	<10	<10	7
1,2-dichlorobenzene	<10	<10	23 ± 6
1,4-dichlorobenzene	<10	<10	3
2,4-dimethylphenol	14 ± 2	<10	5 ± 2
Bis (2-chloroethoxy) methane	<10	<10	31 ± 26
Naphthalene	<10	<10	29 ± 3
Nitrobenzene	<10	<10	20 ± 16
N-nitrosodiphenylamine	11 ± 6	<10	<10
Phenol	180 ± 160	14 ± 8	660 ± 160
Pentachlorophenol	40 ± 35	<10	30 ± 10
Bis (2-ethylhexyl) phthalate	16 ± 10	4 ± 1	17 ± 2
Di-n-butyl phthalate	42 ± 2	90 ± 47	420 ± 390
Diethyl phthalate	<10	<10	34 ± 12
Dimethyl phthalate	20 ± 14	<10	<10
Miscellaneous			
Asbestos (10^6/liter)	NA	NA	NA
Cyanide (µg/liter)	NA	NA	240
Phenol (mg/liter)	NA	NA	3.3
Trace metals (mg/liter)			
Antimony	0.008	0.003	0.005
Arsenic	0.004	0.004	0.006
Beryllium	0.0001	0.0002	0.0001
Cadmium	0.018	0.008	0.026
Chromium	0.22	0.090	0.43
Copper	0.14	0.050	0.29
Mercury	0.0003	0.0001	0.001
Manganese	0.07	0.048	0.09
Nickel	0.20	0.22	0.27
Lead	0.11	0.003	0.11
Selenium	0.007	0.007	0.006
Silver	0.005	0.002	0.005
Thallium	<0.0001	0.001	0.001
Zinc	0.37	0.26	0.44

a. Values for general and miscellaneous parameters are from 1977-78 monitoring data.
b. Final effluent includes centrate (0.03×10^{11} liters/year).

	Los Angeles City[b]			Orange County[c]			San Diego City
	Primary	Secondary	7-Mile Sludge	Primary	Secondary	Centrate	Primary
Flow (liters/yr x 10^{11})	4.47	1.38	0.064	2.64	0.40	0.0097	1.7
pH	7.2[d]	7.4[d]	7.3[d]	7.3	7.3	7.9	6.9
General Constituents (mg/liter)							
Total suspended solids	82	4	12,000	54	7.1	153	165
Oil and grease	25[d]	2.1[d]	580[d]	14	0.6	<5	40
Ammonia nitrogen	21	7.2	280	42	5.7	630	22
Nitrate nitrogen	0.33	3.1	NA	0	3.7	0	<0.01
Total (K) nitrogen	31	9.5	740	48	8.3	630	36
Total phosphorus	8.0	0.7	220	1.7	2.4	41	7.4
BOD	200[d]	9[d]	4,700[e]	160	8.8	80	230
COD	340[d]	27[d]	8,700[e]	NA	NA	NA	260
Fecal coliform (MPN/100 ml)	21 x 10^6	93 x 10^3	3.9 x 10^6	3.4 x 10^7	1.1 x 10^4	4.9 x 10^5	80 x 10^6[f]
Volatile Organics (µg/liter)							
Benzene	28 ± 13	<10	<10	<10	<10	<10	<10
1,1-dichloroethane	14 ± 5	<10	<10	16 ± 1	<10	15	<10
1,1,1-trichloroethane	340 ± 250	<10	<10	4,000 ± 2,700	<10	<10	68 ± 6
1,1,2-trichloroethane	<10	<10	<10	20 ± 15	<10	<10	<10
Chloroform	47 ± 17	26 ± 20	<10	20 ± 2	<10	<10	12 ± 1
1,1-dichloroethylene	20 ± 6	<10	<10	1,600 ± 400	<10	<10	<10
1,2-trans-dichloroethylene	8 ± 4	<10	145 ± 5	<10	<10	44	<10
Ethylbenzene	120 ± 76	<10	16 ± 0	45 ± 45	<10	<10	<10
Methylene chloride	410 ± 200	14 ± 1	<10	100 ± 5	<10	<10	<10
Tetrachloroethylene	290 ± 120	<10	<10	190 ± 0	<10	<10	70 ± 0
Toluene	310 ± 150	<10	30 ± 13	28 ± 2	<10	<10	<10
Trichloroethylene	160 ± 40	<10	<10	37 ± 1	<10	350	12 ± 1
Extractable Organics (µg/liter)							
2-chlorophenol	<10	<10	8 ± 3		[<10]		<10
4-nitrophenol	<10	<10	90 ± 80		[<10]		<10
Phenol	32 ± 8	<10	700 ± 60		(16 ± 9)		260 ± 20
Pentachlorophenol	<10	<10	<10		(25 ± 0)		<10
Bis (2-ethylhexyl) phthalate	<10	10 ± 6	13 ± 8		(48 ± 14)		<10
Miscellaneous							
Asbestos (10^6/liter)	40 ± 1	0.9 ± 0.2	11,000 ± 0		(10 ± 4)		320 ± 100
Cyanide (µg/liter)	29 ± 4	10 ± 0	300		(2 ± 0)		<10
Phenol (mg/liter)	0.10 ± 0.01	0.006 ± 0	0.24		(0.042 ± 0.018)		0.26 ± 0.02
Trace Metals (mg/liter)							
Antimony	0.04	0.05	0.23		(0.10)		0.12
Arsenic	0.01[d]	0.01[d]	0.20[d]		(0.005)		0.014
Beryllium	0.001	0.001	0.002		(0.001)		0.001
Cadmium	0.02[d]	0.01[d]	1.3[d]	0.021	0.025	0.005	0.004
Chromium	0.18[d]	0.03[d]	12.8[d]	0.045	0.049	0.026	0.15
Copper	0.25[d]	0.03[d]	15.5[d]	0.042	0.082	0.084	0.19
Mercury	0.003[d]	0.002[d]	0.13[d]		(0.0003)		0.002
Manganese	0.06[d]	0.05[d]	0.80[d]		(0.048)		0.23
Nickel	0.20[d]	0.15[d]	4.1[d]	0.31	0.18	0.08	0.082
Lead	0.03[d]	0.02[d]	2.2[d]	0.02	0.03	0.04	0.11
Selenium	0.002	0.003	0.069		(0.002)		0.003
Silver	0.03[d]	<0.01[d]	1.9[d]	0.003	0.005	0.004	0.021
Thallium	0.010	0.017	0.065		(0.018)		0.026
Zinc	0.40[d]	0.17[d]	28[d]	0.061	0.09	0.046	0.03

a. Certain values, as indicated in the footnotes below, are based on analyses of samples not collected in July 1978.
b. The average 5-mile effluent in 1977 (4.41 x 10^{11} liters/yr) was approximately 60 percent primary and 40 percent secondary effluent.
c. When only one value is given for this discharger (in parentheses), it is an estimate for the 1983 projected effluent.
d. 1977 average from treatment plant monitoring data.
e. Sample collected 18 Jan 1972.
f. Average for 1977-78 from treatment plant monitoring data.

Table . Concentrations (mean ± standard error) of EPA Priority Pollutants in the effluents of Los Angeles City, Orange County, and San Diego City, based on analysis of 24-hour composite or grab samples collected in July 1978[a] (NA means “not analyzed”).