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EP; January 1983 Change 2

TREATABILITY MANUAL

VOLUME V. Summary

OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

September 1981 (Revised 8/31/82) (Revised 1/24/83)

INSTRUCTIONS FOR UPDATE OF VOLUME V, TREATABILITY MANUAL CHANGE 1 AND CHANGE 2 (1/24/83)

	Section	Instruction	Sheets (front/back)	Revision Status
	List of Instructions	Replace entire section with instructions provided		Change 2
	Table of Contents	Replace the following sheets with revised sheets provided:	v	Change 2
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v.5	References		v.5-1/2	Change 2
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V.6	MB/DAK and Cross References	Replace the Bibliography with the following new section:	v.6	Change 2
V.7	Data Interpretation	Replace the following sheets with revised	V.7-3/4	Change 2
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			v.7-25/26	Change 2
		Add the following new sheet	V.7-49a	Change 2
		Replace the following sheets with revised sheets provided:	v.7-65/66	Change 2
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V.A	Appendix A	Replace the following sheets with revised	V.A-1/2	Change 2
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PREFACE

In January, 1979, USEPA's Office of Enforcement and Office of Water and Waste Management requested help from the Office of Research and Development in compiling wastewater treatment performance data into a "Treatability Manual."

A planning group was set up to manage this activity under the chairmanship of William Cawley, Deputy Director, Industrial Environmental Research Laboratory - Cincinnati. The group includes participants from: 1) the Industrial Environmental Research Laboratory - Cincinnati; 2) Effluent Guidelines Division; 3) Office of Water Enforcement and Permits; 4) Municipal Environmental Research Laboratory - Cincinnati; 5) R.S. Kerr, Environmental Research Laboratory - Ada; 6 Industrial Environmental Research Laboratory - Research Triangle Park; 7) WAPORA, Incorporated; and 8) Burke-Hennessy Associates, Incorporated.

The objectives of this program are :

- to provide readily accessible data and information on treatability of industrial waste streams;
- to provide a basis for research planning by identifying gaps in knowledge of the treatability of certain pollutants and waste streams.

The primary output from this program is a five volume Treatability Manual. This was first published in June 1980, with revisions made in September 1981 and August 1982. This publication replaces Volume I in its entirety, and updates Volumes II, III, IV, and V. The individual volumes are named as follows:

Volume I - Treatability Data

Volume II - Industrial Descriptions

Volume III - Technologies

Volume IV - Cost Estimating (In the process of re-

vision for later publication)

Volume V - Summary

ACKNOWLEDGEMENT

The development of this revision to the Treatability Manual has resulted from efforts of a large number of people. It is the collection of contributions from throughout the Environmental Protection Agency, particularly from the Office of Water Enforcement, Office of Water and Waste Management, and the Office of Research and Development. Equally important to its success were the efforts of the employees of WAPORA, Inc., and Burke-Hennessy Associates, Inc., who participated in this operation.

A list of names of contributors would not adequately acknowledge the effort expended in the development of the manual. This document exists because of the major contributions of numerous individuals within EPA and the EPA contractors, including:

Effluent Guidelines Division
Office of Water Regulations and Standards, Office of
Water

Permits Division
Office of Water Enforcement and Permits, Office of
Water

National Enforcement Investigation Center
Office of Enforcement

Office of Research and Development

Center for Environmental Research Information

Municipal Environmental Research Laboratory

Robert S. Kerr Environmental Research Laboratory

Industrial Environmental Research Laboratory
Research Triangle Park, NC

Industrial Environmental Research Laboratory Cincinnati, OH

As Committee Chairman, I would like to express my sincere appreciation to the Committee Members and others who contributed to the success of this effort.

William A. Cawley, Deputy Director, IERL-Ci Chairman, Treatability Coordination Committee

Date: 1/24/83



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Master Bibliography/Document Access Key

The Master Bibliography/Document Access Key is a central file for all references obtained in the development of the Treatability Manual. The list includes over 600 references. Reference cites include, as standard information, a microfiche number and volume reference cites, on the first line. The second line contains further identifiers in the form of EPA document or contract numbers, PB numbers, Library of Congress numbers as well as any other reference specific numbers available. The remainder of the lines are reserved for the reference cite. The individual volume cross-referencing tables are comprised of volume specific reference cites (i.e. 1-2, 3-8) in one column cross-referenced to the appropriate microfiche number from the Master Bibliography.

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preparation of field spikes. Sample splitting represents a division of the sample into two or more portions for parallel analysis by independent laboratories. Splits may be developed for duplicate analysis (e.g., by EPA and the facility) or analysis of specific fractions (e.g., metals, organics). Field blanks represent water samples of known composition that are prepared in the field and handled in a manner similar to the other samples. These are used as a means of characterizing the contamination that occurs during the sample handling. spikes represent the addition of a known quantity of material to the sample in the field. The subsequent analysis of a field spike will identify the changes which occur due to the effect of sample instability as well as the effects due to the analytic method used in the laboratory. The stability effects can be determined by comparing the results of a field spike to the results of a laboratory spike (the laboratory spike characterizes the method effects only).

V.7.2.2 Analysis - General

The basic premise in the development of analytical chemistry techniques is that by establishing a rigorous protocol for the handling and analysis of the sample, the test results will be representative of the true concentration of the tested species within certain, well-defined statistical limits. The chemist may report the value measured in terms of a range, but it is common to present only one value.

The analysis of toxic pollutants in industrial wastewaters is complicated because the chemical nature of the sample may not be known and there usually are a large number of pollutants present. The relative levels and types of priority pollutants may vary at a plant from day-to-day, or even from one shift to another. An analytical method perfectly suited to one wastewater matrix may be less effective in a different matrix, despite the fact that the same priority pollutants, or a similar combination, are being analyzed. However, an industrial category where a relatively invariant wastewater is characteristic may not present this problem.

Quality assurance and quality control (QA/QC) during the analysis of toxic pollutants is required to ensure that all results have been developed using accepted methods and that the quality of the resulting measurements can be estimated. The quality of a particular method is characterized by estimates of the precision of the measurement and the accuracy of any such measurement. (Precision refers to the refinement with which a measurement can be determined. Accuracy refers to the degree to which the measurement conforms to the true concentration within the sample at the time of analysis). Validation of a measurement requires validation of the method by determining both the multiple laboratory operational precision and the pooled single operator precision. Also required is self-validation of the particular method in a given laboratory.

Date: 1/24/83 R Change 2 V.7-3

TABLE 7.2-5. SUMMARY OF OVERALL ANALYTICAL RECOVERIES FOR VARIOUS CLASSES OF PRIORITY POLLUTANTS [5-57]

Compounds	Method Standa	Method Standard Analysis		Matrix Spiked Analysis		
Class/Number	P <u>+</u> Sp/N(a)	Range/L(b)	P <u>+</u> Sp/N(a)	Range/L(b)		
Purgeables/30	90 <u>+</u> 20/785	59-106/4	92 <u>+</u> 27/2161	32-111/4		
Acids/11	84 <u>+</u> 23/360	61-96/4	76 <u>+</u> 26/862	54-102/5		
Base/Neutrals/43	84 <u>+</u> 30/1415	56-142/3	68 <u>+</u> 29/2762	27-105/5		
Pesticides/18	78±16/5 05	65-85/3	59 <u>+</u> 15/960	42-76/4		
Metals/13	108 <u>+</u> 34/385	83-136/2	96 <u>+</u> 26/1638	79-106/3		
Cyanide	103 <u>+</u> 7/65	103-103/2	96 <u>+</u> 14/70	93-101/2		
Total Phenols	101 <u>+</u> 8/58	97-107/3	96 <u>+</u> 11/85	93-98/3		
All Organics/102	85 <u>+</u> 25/3065	56-142/5	73 <u>+</u> 26/6745	32-111/5		

⁽a)N is the total number of measurements used to compute the cited average recovery (P)

and standard deviation (Sp).

(b) The range of average recoveries for the compounds in a class and the number of contributing laboratories (L) is given in this column.

Table 7.2-6. Interlaboratory comparison of percent recovery data for priority pollutant fractions analyzed using the April 1977 EPA protocol (a) [5-57]

Priority Pollutant Fraction(b)	Lab I	Lab II	Lab III	Lab IV	Lab V	Lab VII	Average
Volatile (MS)	88 <u>+</u> 21	95 <u>+</u> 5		100 <u>+</u> 8			90 <u>+</u> 13
Volatile Sample Spike	82 <u>+</u> 24	101 <u>+</u> 9	93 <u>+</u> 13	107 <u>+</u> 9			92 <u>+</u> 15
Acid (MS)	90 <u>+</u> 18	89 <u>+</u> 5		67 <u>+</u> 14	82 <u>+</u> 16		84 <u>+</u> 13
Acid Sample Blank	92 <u>+</u> 34	72 <u>+</u> 10	62 <u>+</u> 12	60 <u>+</u> 15	84 <u>+</u> 17		76 <u>+</u> 19
B/N-(MS)	95 <u>+</u> 25	78 <u>+</u> 41		77 <u>±</u> 15			84 <u>+</u> 25
B/N Sample Spike	84 <u>+</u> 18	61 <u>+</u> 22	55 <u>+</u> 24	68 <u>+</u> 16		63 <u>+</u> 13	68 <u>+</u> 21
Pesticide (MS)	73 <u>+</u> 8	74 <u>+</u> 19		88 <u>+</u> 8			78 <u>+</u> 11
Pesticide Sample Spike	69 <u>+</u> 7	51 <u>+</u> 18	33±10	93 <u>+</u> 5			59 <u>+</u> 11
Metals (MS)	113 <u>+</u> 37			103 <u>+</u> 8			108 <u>+</u> 22
Metals Sample Spike	100 <u>+</u> 20	103 <u>+</u> 14		92 <u>+</u> 7			96 <u>+</u> 11
Cyanide (MS)	103 <u>+</u> 14			103 <u>+</u> 8			103 <u>+</u> 7
Cyanide Sample Spike	101 <u>+</u> 12			93 <u>+</u> 16			96 <u>+</u> 14
Phenolics (MS)	10 <u>+</u> 13	97 <u>+</u> 6		100 <u>+</u> 7			101 <u>+</u> 8
Phenolics Sample Spike	93 <u>+</u> 15	98 <u>+</u> 10		97 <u>+</u> 9			96 <u>+</u> 11

⁽a) The values are in units of percent recovery plus or minus (±) one standard deviation. Percent recovery and standard deviation are weighted averages based on the number of data points contributed by each laboratory.

tributed by each laboratory.

(b) MS refers to the method standard or the standard addition to blank water. Sample spike refers to the standard addition to a sample.

This indicates that most data are probably reported at concentra tion lower than actually existed.

June 1977 EPA Protocol

The June 1977 EPA protocol included a QA/QC requirement similar to that required for the April 1977 protocol. The precision and accuracy of the data developed using this protocol have not been defined by the sources used in preparing this manual.

December 1979 EPA Protocol

This protocol includes as a fundamental requirement the validation of the analytic methods prior to their use for routine analysis of a wastewater matrix. EPA is sponsoring validation studies that are to establish the accuracy and precision of the methods. However, these studies have not been completed.

The protocol also includes a requirement that each laboratory establish control limits for evaluating the reliability of the methods during routine analysis. The sources of data used in this manual have not reported any results of these laboratory-specific validation and QA/QC programs.

An evaluation of the precision, bias and comparability of the inductively coupled plasma method ICP with that of flame atomic adsorption AA was made by the EPA Effluent Guidelines Division in 1980 for total metals (iron, chromium, copper, nickel, lead and zinc) in mine effluents. This study, while limited in scope, was an inter-laboratory round-robin conducted in accordance with ASTM D2777-77, "Standard Practice for Determination of the Precision and Bias of Methods of Committee D-19 on Water." The limits of detection and of determination in mine effluents based on interlaboratory precision for the ICP method were several times higher than those for flame AA in the O-1 mg/L range for all of the above mentioned elements except chromium.

Date: 1/24/83 R Change 2

3. RBC Pilot Scale Study

Sampling: Swanson - Oswald Assc. Analysis: Swanson - Oswald Assc.

Reference: 5-62

Date: November 1977 - March 1978

Procedures: Data Set 3 - RBC Pilot Scale Study

A pilot scale study of rotating biological contactors was conducted at a gum and wood chemicals manufacturing plant. Sampling and analysis followed standard methodology, outlined in Standard Methods for the Analysis of Water and Wastewater, 14th edition, American Public Health Organization, with a few modifications.

Sampling consisted of, at the minimum, bi-weekly grab samples. Collected samples were preserved on ice until arrival at the laboratory. Pollutant analysis consisted of standard method procedures from the above mentioned protocol as well as parallel and additional analysis using other established methods. The purpose of multiple analysis was to quantify the accuracy of methods chosen when presenting data as well as to further develop the data base. Data are a representation of these analytical methods without analysis specific designation.

Date: 11/8/82 Change 2 V.7-49a

Procedures: Data Set 2 - Additional Sampling (Screening)

The additional screening study was conducted in 1979. The April 1977 EPA protocol was followed for all sampling and analysis work performed during this study. Nine of the thirteen subcategories were included in the study. The survey was initiated in order to determine the concentration of toxic compounds in the industry's raw wastewater.

Procedures: Data Set 3 - Pilot Plant Study

This study was initiated in order to determine the effectiveness of the rotating biological contactor in pollutant removability. The sampling method was unspecified.

Analysis of organics utilized a gas chromatograph with a flame ionization detector, using methods defined by American Society for Testing Materials, Methods D-3328-#aT and D-3257-73, USA. Atomic absorption was used for metals analyses. The organics QA/QC program included the spiking of raw wastewater samples with the organic species to confirm detectability by the method used.

V.7.3.31 Steam Electric Power Plants

Volume II Reference: Section II.19

Data Sets:

Initial BAT Survey (Screening Phase)

Sampling: Hittman Associates, NUS Corporation

Analysis: Carborundum Reference: 5-31

Date: 1977

BAT Survey (Verification Phase)

Sampling: Hittman Associates

Analysis: Richardson Associates, EPA

Reference: 5-31

Date: 1977

Surveillance and Analysis

Sampling: EPA Regional Teams

Analysis: EPA Reference: 5-31 Date: Unspecified

Procedures: Data Set 1 - Initial BAT Survey (Screening

Phase)

The program included analysis at eight plants. The EPA study was paralleled by the electric power industry, including the separate sampling and analysis by industry-contracted laboratories.

V.7-65 Date: 9/25/81

Sampling involved the collection of grab samples and 24-hour composite samples using automatic equipment. The April 1977 EPA protocol was used for sampling.

Analysis used analytical procedures that included the GC/MS for organic pollutants and the AA for metals.

<u>Procedures</u>: Data Set 2 - BAT Survey (Verification Phase)

Sixteen plants were included in this program initially with two plants added later to the data base by EPA, since the data were collected by similar methods and format.

Sampling was performed using the April 1977 EPA protocol. The collected samples were split with the power industry for their parallel analysis. The analytic methods used included the GC/MS or GC for the organic priority pollutants. The inorganics were analyzed by AA or inductively coupled plasma ICP. Mercury was analyzed by cold-vapor AA, selenium by fluorometry, and cyanide by a colorimetric procedure.

Procedures: Data Set 3 - Surveillance and Analysis

The EPA regional Surveillance and Analysis program included periodic visits to power plants to determine compliance with NPDES permits. Priority pollutant sampling was conducted at eight plants. The sampling and analysis procedures were similar to those used in the screening and verification programs. Analytical methods included GC/MS for organics and ICAP for inorganics.

V.7.3.32 <u>Textile Mills</u>

Volume II Reference: Section II.20

Data Sets:

- 1. Comprehensive Field Sampling Program (Screening and Verification Survey, Four Phases)
 - a. <u>Phase 1</u> Joint ATMI/EPA Mobile Plant Project Sampling: ATMI; Monsanto Research Corporation (MRC)

Analysis: ATMI; MRC

Reference: 5-32

Date: March - May 1977

b. Phase 2 - Untreated and Treated Wastewater plus Pilot Plant Advanced Treatment Sampling: Sverdrup and Parcel; EPA Analysis: MRC

Date: 1/24/83 R Change 2 V.7-66

4. Pilot Plant Study

Sampling: CARRE, Inc.

Analysis: Clemson University, Texidyne

Reference: 5-61

Date: Sept. 23, 1977 - Sept. 22, 1978

Procedures: Data Set 4 - Pilot Plant Study

This data set is comprised of pilot plant data generated in the 1978 hyperfiltration study conducted at a La France Industries textile mill. Sample analysis followed standard procedure.

Sampling consisted of one gallon plastic bottle samples collected periodically and sent to the lab for analysis.

Analysis of membrane flux, color and conductivity rejections were monitored on site. Color comparisons where determined through the use of a Bausch and Lomb Spectronic 20 while conductivity measurements were made using a Balsbaugh conductivity bridge and dip cell. All other samples were collected and delivered to the laboratory where analysis was done in accordance with quality assurance procedures approved for this project.

Date: 11/12/82 Change 2 V.7-68a

APPENDIX A NUMBER OF SOURCE/TREATMENT TECHNOLOGY DATA SETS

Date: 9/25/81

TABLE A-1. NUMBER OF SOURCE/TREATMENT TECHNOLOGY DATA SETS

	Data Sets		
	Full	Pilot	Bench
Industry/control technology	scale	scale	scale
Adhesives and sealants			
Chemical oxidation		1	
Reverse osmosis		1	
Sedimentation		1	
Auto and other laundries			
Activated carbon adsorption-granular	1	1	
Chemical precipitation	ī	_	
Filtration	3		
Flotation	10		
Ultrafiltration	10	5	
Cool wining			
Coal mining	7		
Sedimentation	,	1	
Rotating biological contactors		1	
Coil coating			
Chemical precipitation	6		
Filtration	1		
Sedimentation	2		
Inorganic chemicals manufacturing			
Chemical oxidation	2		
Chemical precipitation	5		
Chemical reduction	1		
Filtration	4		
Sedimentation	3		
Stripping-air	1		
Iron and steel manufacturing			
Chemical precipitation	1		
Coagulation and flocculation	5		
Filtration	4		
Neutralization	1		
Oil separation	1		
Sedimentation	8		
Solvent extraction	1		
Ultrafiltration	1		
Activated sludge	1		
Leather tanning and finishing			
Sedimentation	1		
Activated sludge	8		
Lagoon	2	1	
Trickling filters	1		

TABLE A-1. NUMBER OF SOURCE/TREATMENT TECHNOLOGY DATA SETS (CONTINUED)

	Data Sets		
Industry/gentral technology	Full scale	Pilot scale	Bench scale
Industry/control technology	Scare	SCATE	2016
Battery manufacturing			
Chemical precipitation	1		
Electrical and electronic components			
Activated carbon adsorption-granular	1		
Chemical precipitation	ī		
Chemical reduction	1		
Coagulation and flocculation	1		
Filtration	3		
Oil separation	1		
Foundries			
Chemical precipitation	1		
Filtration	1		
Sedimentation	9		
Metal finishing			
Chemical precipitation	28		
Chemical reduction	5		
Reverse osmosis		1	
Sedimentation	2		
Aluminum forming			
Chemical precipitation	1		
Chemical reduction	1		
Coagulation and flocculation	2		
Oil separation	2		
Sedimentation	1		
Ultrafiltration	1		
Copper forming			
Chemical precipitation	3		
Filtration	1		
Plastics processing			
Activated sludge	1		
Porcelain enameling			
Chemical precipitation	1		
Gum and wood chemicals			
Activated carbon adsorption-granular	1		
Sedimentation	ī		
Lagoon	3		
Rotating biological contactor	_	2	
Date: 1/24/83 R Change 2 V.A-3			

TABLE A-1. NUMBER OF SOURCE/TREATMENT TECHNOLOGY DATA SETS (CONTINUED)

		Data se	ts
	Full	Pilot	Bench
Industry/control technology	scale	scale	scale
Pesticide manufacturing Activated carbon adsorption-granular	1		
Pharmaceutical manufacturing Activated sludge Lagoon-aerated	3 2		
Nonferrous metals manufacturing Chemical precipitation	2		
Ore mining and dressing Activated carbon adsorption-granular Chemical oxidation Chemical precipitation Filtration Ion exchange Sedimentation	1 6 1 14	1 2 4 5 1 2	
Organic chemicals Activated carbon adsorption-granular Chemical oxidation Ion exchange Stripping-steam Solvent extraction	1	14 3 6 13	
Paint and ink formulation Chemical precipitation Filtration Sedimentation Lagoon	11 2 3 1		
Petroleum refining Activated carbon adsorption - powdered Activated carbon adsorption - granular Filtration	1	4 6 6	2
Flotation Flotation Solvent extraction	1	4	

TABLE A-1. NUMBER OF SOURCE/TREATMENT TECHNOLOGY DATA SETS (CONTINUED)

	Data Sets		
	Full	Pilot	Bench
Industry/control technology	scale	scale	scale
Pulp and paperboard mills			
Activated carbon adsorption			
- Powdered	1		
- Granular		1	
Filtration	1		
Flotation	1		
Activated sludge	2		
Trickling filter	1		
Rubber processing			
Ultrafiltration		2	
Activated sludge	1		
Soap and detergent manufacturing			
Rotating biological contactor		1	
Steam electric power plants			
Chemical precipitation	1		7
Reverse osmosis			6
Sedimentation	2		
Textile mills			
Activated carbon adsorption			
- Powdered	1		10
- Granular		12	
Chemical oxidation		2	
Chemical precipitation	1	3	2
Coagulation and flocculation		2	
Filtration	, 1	12	
Flotation	1		
Reverse osmosis		11	
Ultrafiltration		3	
Activated sludge	33		
Lagoon	4	_	
Sedimentation		1	
Timber products processing		_	
Reverse osmosis		1	
Ultrafiltration	-	1	_
Activated sludge	1		2
Lagoon	1	_	
Trickling filter		2	

Date: 1/24/83 R Change 2 V.A-5

TABLE A-1. NUMBER OF SOURCE/TREATMENT TECHNOLOGY DATA SETS (CONCLUDED)

	Data sets		
	Full	Pilot	Bench
Industry/control technology	scale	scale	scale
Miscellaneous and Unspecified			
Activated carbon adsorption-granular		1	
Solvent extraction		2	•
Activated sludge	1	1	
Organic and inorganic			
Chemical oxidation			1
Chemical precipitation		1	
Filtration		1	
Activated sludge	2		
Totals	248	133	30