

**HAZARDOUS WASTE DIVISION
MEMORANDUM**

TO: Files
THRU: Joe Hoover
FROM: David Brown
DATE: January 27, 1997, revised February 3, 1997
SUBJECT: Ethyl Corp., (Albemarle), South Plant, Magnolia, AR
EPA ID No. ARD052528809
CSN 14-0193 & CSN 14-0028

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Please note that the following alleged violations are not in response to a CEI or any other site visit by the ADPC&E. I have completed a file review regarding operations at the Ethyl South Plant, Pond Solids Vault No. 1, (PSV-1), located in Magnolia, Columbia County, Arkansas. As requested the following supplemental information is provided:

- 1. From 09-16-88 through 05-08-90, Ethyl Corp., disposed of a non-wastewater solid waste contaminated with a hazardous § 268, Appendix III, halogenated organic compound "methyl bromide (bromomethane, CAS 74-83-9)" at suspected concentrations above the statutory level of 1,000 ppm in alleged violation of the California Land Disposal Prohibition § 268.32(e)(2) and § 268.32(f).**

On 06-30-87, Ethyl Corp., requested authorization to dispose of trash and floor sweepings generated from the brominated organic derivatives process areas NC-14, NC-12 & NC-16, with a projected volume of 3.0 tons/day or 105 yd³/wk. On 09-16-88, the ADPC&E, SWD, granted Ethyl authorization to dispose of trash and floor sweepings generated from process areas NC-14, NC-12 and NC-16 into landfill 232-S. Process area solid wastes as generated could possibly have contained various amounts of TBBPA and other process losses.

Listed waste K131 and K132 as provided for in the 10-06-89, Final Rule, would have been expected to contain methyl bromide (bromomethane) concentrations of 50,000 ppm and 15,000 ppm respectively, along with various other brominated compounds (*i.e. Hbr & Bisphenol-A*).

Due to the presence of methyl hydrogen sulfate and sulfuric acid, K131 wastewater would have had a pH of less than 2.0, (see FR, 50, 04-25-85, 16432) meeting the definition for D002 under § 261. Solid wastes containing HOCs are only restricted under the § 268.32 prohibitions if the solid waste is listed or characteristic as defined under § 261. However, the waste listing or characteristic need not be related to HOC content, (see FR, 52, 07-08-87, 25770).

- 2. Disposal of waste filter cake sludge K132 (from April, 1990 to July, 1991) and waste filter cake sludge F005 (from April, 1991 to July, 1991), as generated by the Extraneous Wastewater Project, into landfill (PSV-1), in alleged violation of § 270.1(c).**

The Extraneous Wastewater System draws process waste waters from South Plant production areas NC-16, NC-14, NC-12 and the Bromine Recovery Unit (BRU). Pursuant to the derived from rule § 261.3, extraneous wastewater filter cake sludge would have met the definition for a listed waste K132 and F005. Unable to confirm the existence of verifiable analyses, waste characterization and/or waste identification (see § 262.11), for generated extraneous wastewater filter cake sludge. In July, 1991, Ethyl ceased active disposal operations at PSV-1.

Attachment: Background Information
file name e:\brownd\3025-mem.05

Bromine Recovery Unit (BRU), Background Information:

The BRU is also a Halogen Acid Furnace.

Unit was not in existence prior to 03-14-79. Tank T-621 was built in 1965.

Originally permitted under Air permit 933-A, issued 02-13-89.

Ethyl DOCC, prepared June 1992, revised March 1993:

Per the DOCC, brominated organics from various sources are combusted, in the BRU, for bromine recovery. An aqueous stream, from the BRU's quench tower (C-613), containing sodium carbonate and sodium bromide is processed in the extraneous water system, (see Table 2-1 and Fig 2-7). This aqueous waste stream would carry an F005 waste determination.

BRU enter BIF certification proceedings on 09-21-91, under RCRA. Air Emission Inspection Data collected 12-29-92, in accordance with §264 and §265, subsection BB, indicates that the BRU was managing HBCD by-product at that time, (see Ethyl part B application, appendix W).

HBCD by-product processed by BRU from January 1992 thru July 1992, averaged 9621.5 gals/month.

Ethyl Part B permit application April, 1991, revised 02-04-94:

BRU daily processing rate (1.20 gpm) or 155,520 gals/day.

BRU operates approximately 8,000 hrs/yr.

BRU generates SF-611/Filter/BRU Burner Solids (D001/F005) from the burning of HBCD by-products and is drummed.

BRU receives TBBPA reacidification bottoms (D001/F003).

BRU receives NV Organics from bromine production unit (D002/D042).

BRU receives HBCD by-products (D001/F005) containing brominated solids from recovery of spent IBA solvent, which is received by tanker trailer from the Ethyl West Plant. The HBCD by-product is off-loaded into BRU feed tanks, (see Ethyl part B application, appendix D, B-2 and Dwg 14130000ME0502).

BRU feed tank T-621, capacity 17,000 gals, built 1965, first managed RCRA waste 1988.

Feed tanks D-8222 & D-8223, combined capacity 12,000 gals, are scheduled to replace current BRU feed tank T-621.

Bromine in the BRU's off-gases is captured and returned to the Bromine Plant. HBCD by-product is fed to the by-product burner R-612. HBCD by-product (D001/F005) is feed to the R-612 burner at 1.20 gpm.

Burner R-612 off-gases enter the quench tower C-613 where Hbr and Hcl are removed. Quench tower bottoms are maintained in a liquid state. An organic amine stabilizer is added to the quench tower bottoms, which are then pumped to the recycle bromines tank T-3046 in Area 1, (see Confidential Dwg 14130000FE2105).

Air Permit 762-AR-9, issued 01-26-96.

HBCD By-Product:	HBCD isomers	35%
	Isobutyl alcohol	45%
	Dibromomethane	08%
	Isobutyl isobutyrate	05%
	Isobutyl bromide	04%
	Alkyl amines	03%
	Flash point	less than 140 deg F.

Additional reference, BRU, RCRA, Compliance Test Plan, 10-15-93.

Extraneous Wastewater Project, Background Information:

Response to Ethyl letter dated 06-30-87. ADPC&E, SWD, memo dated 08-27-87, w/attachments D-1 thru D-4, identifies the various Ethyl process and operational areas (including spills and leaks) that feed waste water to the Extraneous Wastewater Project for chemical/physical treatment. The filter cake sludge to be disposed of in (232-S) PSV-1.

ADPC&E, SWD, letter dated 09-16-88, (unable to locate signed copy), response to Ethyl Corp., letter dated 06-30-87, requesting landfill 232-S disposal authorization:

- 1) Authorized disposal of de minimis losses of Extraneous Water Project solid filter cake (unable to locate sludge analysis),
- 2) Prohibited disposal of West Plant Brine Recycling Tank Bottom Sludge,
- 3) Authorized disposal of misc trash and floor sweepings containing brominated organic derivatives (see SW Permit 164-S for descriptions and attachments to 06-30-87, Ethyl letter.), and
- 4) South & West Plants, Clear completion fluid (CCF) filter cake.

Extraneous Water System, Water Permit No. 3532-W, issued 02-01-88, modified 07-06-92.

The ADPC&E, Water Division possess limited analytical information concerning extraneous wastewater project discharges to Ethyl's UIC.

ADPC&E, HWD, memo dated 09-10-87, Subj: K117 (wastewater from the reactor vent gas scrubber from the production of ethylene dibromide-EDB) wastewater generation, Extraneous Water Project, Production Wastewater Treatment, and EDB Recycling.

RADIAN Corp., letter dated 03-07-91 & Ethyl letter dated 06-28-91, w/attachments argued that Ethyl Corp., did not generate K117 waste.

EPA failed to identify any K117 generation, (see FR, 57, 01-09-92, 1001).

Class I, UIC, LDR exemption under HSWA, (see FR, 57, 03-31-92, 10897 and § 148.12 (b)).

K131 and K132, Background Information:

Ethyl Corp., Magnolia, Arkansas began methyl bromide production on or about December, 1983.

HSWA of 1984 required EPA to list in generic terms solid wastes resulting from the production of organobromines. For the purposes of implementation, HSWA defined land disposal as, but not limited to, the placement of prohibited waste in a landfill or surface impoundment. Land disposal prohibitions are effective when promulgated unless the Administrator grants a variance and establishes a differing date, which is not to exceed two years.

The proposed listings (see FR 50, 04-25-85, 16432), K131 wastewater from the reactor and acid drier from methyl bromide production, and K132 spent absorbent and wastewater separator solids from methyl bromide production.

LDR standards were not established by EPA under FR, Final Rule, 54, 10-06-89, 41402.

Wastewater (K131) generated *in* the methyl bromide production reactor is properly designated as wastewater *from* the reactor and therefore meets the listing description (see Final Rule, FR, 54, 10-06-89, 41403).

Methyl bromide production waste code listings K131 and K132 became effective on 04-06-90.

Limited stay of K131 reactor wastewater on 10-22-90. The stay did not extend to K132 or to spent sulfuric acid, from the acid dryer, as generated by Ethyl.

Proposed concentration based treatment standards ethylene dibromide wastes K117, K118, K136, and methyl bromide wastes K131, K132, (see FR, 57, Proposed Rule, 01-09-92, 966-967).

Specific LDR treatment standards for K131 and K132 were effective 11-09-92, (see § 268.36). Land disposal restricted wastes may only be land disposed if they meet applicable treatment standards. The Soft Hammer provisions of RCRA were not applicable to K131 and K132.

California Rule, Background Information:

All such wastes containing California constituents were prohibited from land disposal at concentrations above statutory levels. However, the EPA granted a two year capacity variance starting on 07-08-87, for those regulated HOC wastes, requiring incineration (see FR, 52, 07-08-87, 25760), in land disposal units that met the requirements of § 268.5(h)(2).

The Point-of-Disposal approach is inconsistent with EPA's concerns regarding dilution under § 268.3 of California List Wastes. If a solid waste is not considered restricted until disposal, then by definition it would not be subject to LDR prior to its disposal or dilution. California List Wastes were restricted at the Point-of-Generation, (see FR, 52, 07-08-87, 25765).

As provided for in the Final Rule, FR, 54, 10-06-89, 41402, effective 04-06-90, EPA anticipated constituent concentrations of 0.5% dimethyl sulfate, 5.0% methyl bromide in K131, and 1.5% methyl bromide in K132.

Prior to the 04-06-90, K132 and K131 land disposal prohibition effective date, the waste specific prohibitions pursuant to California List Wastes § 268.32, (see FR 51, 05-28-86, 19305, and California Final Rule, FR, 57, 07-08-87, 25760, effective 07-08-87) applied prospectively. All hazardous wastes disposed of after their applicable effective dates would be subject to their specific restrictions.

Methyl bromide (bromomethane, CAS 74-83-9), § 268, Appendix III, (see FR, 52, 07-08-87, 25791, for original language).

The applicability of the California Rule, after the 05-08-90, Third-Third Final Rule effective date, (see FR, 55, 06-01-90, 22534 and 22674), would in regards to most newly listed wastes supersede the California Rule.

EPA failed to establish treatment standards for newly listed wastes K131 and K132 by 05-08-90.

SW Landfill Permit No. 232-S (PSV-1), Background Information:

Ethyl Corp., letter dated 07-01-85, RE: Landfill 232-S, Permit Modifications, identification of TBBPA found in pond solids at 200 ppm. Assumed tribromophenol concentration of 1.4 ppm.

Ethyl Corp., letter 10-01-86, original design capacity 200,000 cu.ft assuming 70% at 65 lbs/cu.ft.

ADPC&E, Solid Waste, Class III Landfill, Permit No. 232-S (PSV-1), effective 04-17-87. PSV-1 was constructed in accordance with the Arkansas Solid Waste Management Code (Act 237 of 1971, A.C.A. § 8-6-201, et. seq.).

Process area losses as provided under Ethyl Corp., letter 06-30-87, estimated at 3.0 tons/day. These losses were disposed of in landfill 232-S (PSV-1).

Ethyl Corp., letter dated 10-21-87, request to dispose of West Brine Tank Sludge in landfill 232-S.

ADPC&E, HWD, memo, 09-10-87, provided that even *de minimis* losses of a listed waste or a listed commercial chemical product would be regulated under RCRA.

ADPC&E, SWD, letter dated 11-19-87, authorization to dispose West Brine Recycling Tank Bottom Sludge in landfill 232-S.

03-02-88, Ethyl Corp., letter to ADPC&E, in response to the suspected disposal of fire retardant in landfill 232-S. Ethyl responded that only incidental quantities of paper were to be disposed of in landfill 232-S.

Ethyl analysis dated 07-31-85, West Brine Recycling Tank Bottom Sludge:

- 1) No Detect (EDB) ethylene dibromide, and
- 2) No Detect (DBCP) 1,2-dibromo-3-chloropropane.

ADPC&E, SWD, letter dated 03-03-89, disposal authorization of a polymeric waste by-product from TBBPA production in landfill 232-S.

ADPC&E, SWD, memo, 05-21-90, disposal of K132 in landfill 232-S.

ADPC&E, letter dated 01-25-94, Permit 232-S (PSV-1), Notification, Transfer of Regulatory Authority.

PSV-1 closed on-or-about September, 1994.

Products, Production Areas and Waste Descriptions:

ADMA	alkyldimethylamine
DBDPO	decabromobiphenyl oxide
DECTP	diethyl chlorothiophosphate
TBBPA	tetrabromo-bis-phenol - A
Hbr	hydrobromic acid as a TBBPA production by-product
EDB	ethylene dibromide (1,2-dibromoethane), CAS 106-93-4

NC-16 1,2 tetrabromophthalimide ethane
tetrabromophthal anhydride.

NC-14 bisphenol - a
TBBPA
TBBPA waste polymer

NC-12 phthalic anhydride
brominated phthalic anhydride
bis (tetrabromophthalimide) ethane

T-9590 PSV-1 leachate storage tank

K132 spent alumina from methyl bromide production, less than 20 ppm methyl bromide.

K132 bromoform leachate wastewater.

K132 waste polymer bromoform, from the TBBPA process.

K117 EDB recycling and extraneous wastewater treatment.

K117 aqueous bottoms from the reactor vent scrubber: methyl bromide (bromomethane)
chloroform (trichloromethane)
EDB, ethylene dibromide (1,2-dibromoethane)

K118 EDB (ethylene dibromide) contaminated alumina and filters, (generation rate approx. 8 cu.ft./month):
methyl bromide (bromomethane)
chloroform
less than 10% by wt. EDB (1,2-dibromoethane)
alumina greater than 90% (see RADIAN, ltr, 03-07-91)

EDB is removed from K118 waste by draining the column, (see RADIAN, ltr, 03-07-91).

Loose newspaper weighs approximately 7.0 lbs/cu.ft. or 189.0 lbs/yd³. EDB weighs approximately 3,673 lbs/yd³.

The following solid wastes and related constituent percent concentrations by weight, per Albemarle Corp., letter dated 12-20-95, and the attached Ethyl, letter dated 12-18-90:

Spent Sulfuric Acid after stripping:	methyl hydrogen sulfate	6.1%
	methanol	0.5% (recycled into TBBPA process reactor)
	dimethyl ether	1.4%
	dimethyl sulfate	0.007% (sulfuric acid, dimethyl ester)
	methyl bromide (bromomethane)	200 ppm
	spent sulfuric acid (K131)	reclaimed off-site
	spent alumina absorbent (K132)	steam stripped and disposed of in PSV-1
	methyl bromide	stored as TBBPA co-product
	reactor vent wastewater (K117)	Class I, UIC for bromine recovery

Alumina after stripping (K132):	methyl bromide (bromomethane)	20 ppm
	hydrogen bromide	trace
	water	trace
	iron bromides	trace.

Enforcement, Background Information :

RCRA part A application, 11-14-80, U067, U077, U154.
RCRA part A application, 12-22-81, U056, U067 (EDB), U077 (dichloroethane), U083, U154.
Notification of Regulated Activity, 04-12-91, BIF and F003, F005, K118, K132, U045, U210, U220.
RCRA part A application, 04-19-91, F001, F003, F005, K118, K132, U220.
RCRA part A application, F002, F003, F005, K131, K132, K118, U220, U045, U210, U154, U067.

Arkansas final authorization, Hazardous Waste Mgt Program, FR 55, No. 59, 03-27-90, 11192.

RQ requirements adjustment methyl bromide production wastes FR, 54, 10-06-89, 41402-41408, (AHWMC Sec. 3(a)2, as amended 10-24-90, effective 12-17-90).

cc: Ali Dorobati, Technical Branch, HWD
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