Chemical Wastes in the Sea: New Forms of Marine Pollution

Abstract. *Drums containing chemical wastes have been found in and along the North Sea. The wastes were analyzed and were found to include lower chlorinated aliphatic compounds, vinyl esters, chlorinated aromatic amines and nitrocompounds, and the insecticide endosulfan. Because dropping these drums into the sea endangers the environment and results in damage to fishing operations, measures should be taken to stop this practice.*

Pollution of the open seas by human activities has long been recognized as a serious problem. In some, although still too few, cases progress has been made in combating its causes and adverse effects (*1*).

A relatively new aspect of this problem is the increasing practice of dropping drums containing chemical wastes, mostly from heavy chemical industries, into the sea. The situation is aggravated by the fact that there is an increasing tendency to deposit these wastes not only in the ocean but also in shallow, intensely fished waters like the North Sea.

In the last few years, approximately 80 samples from drums containing chemical wastes have been brought to the National Institute of Public Health at Utrecht for analysis. Most of the drums were caught by Dutch fishermen during fishing operations on the North Sea and were brought to various harbors in the Netherlands (an example is shown on the cover). Other drums had been washed ashore along the Dutch coast.

In addition, several samples were taken in the harbor of Rotterdam from loads of drums that were being transferred to outbound freighters. The instructions specify that these drums be dropped into the Atlantic Ocean above 65°N, at a minimum depth of 2000 m and at least 100 miles (161 km) from

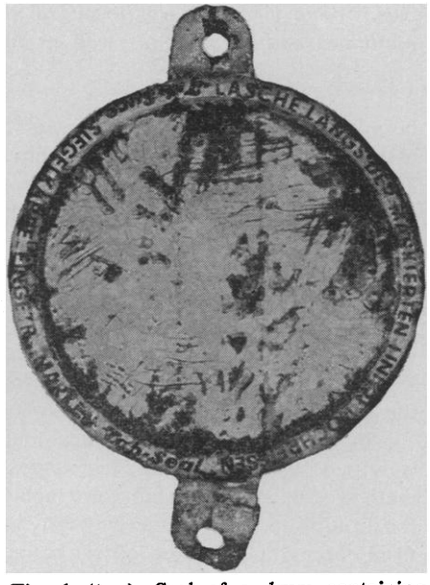

Fig. 1 (top). Seal of a drum containing mixture B (see Table 1). Fig. 2 (bottom). Screw cap of a drum containing mixture D (see Table 1).

Table 1. Composition and toxicity of wastes found in the North Sea (mixtures A, B, C, D, and E_1) and of wastes scheduled for dumping in the sea, ready for loading at Rotterdam harbor (mixtures B, D, E_1, E_2, and F). In each toxicity experiment, three 2-week-old guppies were used. The toxicity is expressed as follows (ppm, parts per million; ppb, parts per billion): −, 100 ppm gives no kill in 3 days; +, 1000 ppm is lethal within 2 hours but 100 ppm gives no kill in 3 days; ++, 100 ppm is lethal within 2 hours but 10 ppm gives no kill in 3 days; +++, 10 ppm is lethal within 2 hours but 1 ppm gives no kill in 3 days; ++++, 10 ppb is lethal within 2 hours but 1 ppb gives no kill in 3 days.

Mixture	Composition: Compound	Composition: Approx. average content (%)	Toxicity	North Sea samples investigated (No.)	Harbor samples: est. total weight of loads (tons)
A	Vinyl acetate and vinyl propionate	90	++	7	
	Phenothiazine	5			
	Isopropenyl acetate	Trace			
	Acetic acid	Trace			
	N-Acetylphenothiazine	Trace			
B	1,2-Dichloropropane	60	+	54	650
	Di(2-chloroisopropyl) ether	25			
	Propylene, butylene, and trimethylene oxides	5			
	Chloropropanoles	5			
	Epichlorohydrin	5			
C	Mineral oils	100	−	4	
D	Endosulfan and derivatives	5	++++	3	350
	Toluene	5			
	Clayish material	55			
	Solution of sodium sulfite, sodium carbonate, and sodium chloride	35			
E_1	Trichlorotoluidines	80	+++	1	350*
	Dichlorotoluidines	15			
	Monochlorotoluidines	Trace			
	o-Toluidine	Trace			
E_2	Dichloronitrobenzenes	85	+++		
	Trichlorobenzenes	Trace			
	p-Dichlorobenzene	10			
F	2-Butene-1,4-diol diacetate	95	+++		
	Hexachlorobutadiene	Trace			
	Dichloropropanoles	Trace			
	Epichlorohydrin	Trace			

* This value is the total for mixtures E_1, E_2, and F.

the coast. Similar drums, however, with the same content, have been found in the North Sea.

The samples were purified by crystallization, distillation, or gas-liquid chromatography. The components were identified by their melting points, and ultraviolet, infrared, or mass spectra. In most cases, more than 90 percent of the contents could be identified. The remainder was tarry or highly polymerized material.

The acute toxicity to fish was estimated by exposing guppies to sequences of decreasing (in powers of ten) dilution of the samples. The results of the chemical and biological investigations are summarized in Table 1.

The samples can be grouped together into a limited number of subgroups, designated mixtures A to F, each of comparable chemical composition and toxicity. The drums containing mixture B can be recognized by their seal (Fig. 1); the drums containing mixture D, by their higher weight and typical screw cap (Fig. 2). None of the samples were measurably radioactive.

Sooner or later, the drums containing the wastes will become corroded and the contents will spill into the sea. The fate of the chemicals in the sea is largely unknown, but from general chemical considerations it can be anticipated that most of the chemicals identified are of a persistent nature. The history of endosulfan (present in mixture D) in fresh surface waters has been studied recently (*2*): its half-life was found to vary, according to circumstances, from 1 week to several months. Although the aqueous phase of the mixture is strongly alkaline, the hydrolysis of endosulfan, which is dissolved in the organic phase, proceeds very slowly. Mixture D, even when diluted to 1 part in 100,000,000, was found to be lethal to fish. Aside from the potential danger to the environment, the drums also damage the fishermen's nets and the fish caught in them. The number of drums dropped into the sea is not known exactly, but reasonable estimates run to several tens of thousands. Plans are currently being made to clear the drums from at least the intensely fished areas and to burn their contents (*3*).

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References and Notes

1. *Water Res.* 4, 259 (1970).
2. P. A. Greve and S. L. Wit, *J. Am. Water Works Assoc.*, in press.
3. The need for international agreements to control the dumping of industrial wastes in the sea was emphasized in a comment on this report by D. L. Kedde, public health officer of the Ministry of Social Affairs and Public Health, Leidschendam, the Netherlands. Appropriate legislation is lacking, he said, and, since the responsibility of industry ends when the drums are loaded on the ship, a loophole exists which permits an all too easy solution to the problem of disposing of chemical wastes. The prevention of this careless practice, in Kedde's opinion, will require international agreements and stringent enforcements. Dumping of drums in fished areas should be absolutely forbidden, he added, because the drums can damage fishing equipment.
4. I thank the departments of mass spectrometry of the Analytical Chemical Laboratory of the State University at Utrecht and the Central Institute for Nutrition and Food Research TNO at Zeist for their assistance.

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[^{3}H]Lysergic Acid Diethylamide: Cellular Autoradiographic Localization in Rat Brain

Abstract. *Intravenous administration of [^{3}H]lysergic acid diethylamide (LSD) to rats resulted in accumulation of the drug in the brain within 15 minutes. Autoradiographic methods were used to differentiate free and bound [^{3}H]LSD in brain tissue. Free [^{3}H]LSD was generally distributed in the pituitary and pineal glands, cerebellum, hippocampus, and choroid plexus. Bound [^{3}H]LSD was localized in neurons of the cortex, caudate nucleus, midbrain, and medulla, as well as in choroid plexus epithelium.*

D-Lysergic acid diethylamide (LSD), the most potent hallucinogenic compound known, produces a multiplicity of pharmacological actions in the central nervous system, which have been postulated to result from stimulation or inhibition of serotonin receptors and possibly to involve neurons containing norepinephrine (*1*). Distribution and localization of LSD in various organs and tissues has been measured in a number of laboratories (*2*). However, most often tissue homogenates of whole organs or specific regions of organs have been used. The results so obtained reflect the total concentration of the compound present in the homogenized fraction but do not permit localization of the compound to individual cells in the regions reported. Metabolic studies of brain tissue in vitro have shown that the brain does not metabolize LSD (*3*); we assume in this report that the cellular localization demonstrated by means of autoradiography is that of LSD. However, the presence of a metabolite circulating from the liver to the brain is not excluded.

The availability of [^{3}H]LSD with high specific activity makes it possible to study cellular localization with high-resolution autoradiography. Because [^{3}H]LSD may exist in tissue in free and bound forms, attempts to localize this compound in tissues by means of conventional histological procedures alone may lead to false results (*4*). The use of solvents for fixation, dehydration, clearing, embedding, and removal of embedding materials should be avoided as should wet photographic tissue mounting for autoradiography. The artifacts likely to occur in a procedure using such compounds result from extraction, leaching, and translocation of the labeled compound during tissue processing (*5*). Therefore, we used the technique of applying freeze-dried frozen sections to dried photographic emulsion developed for the study of diffusible substances (*4–7*); in conjunction with this technique we used a conventional histological method for cellular autoradiographic localization to differentiate between the firmly bound and free or loosely bound forms of [^{3}H]LSD as defined previously (*7*). Autoradiography is a valuable technique used for studying cells within a heterogeneous population (*8*).

D-Lysergic acid diethylamide, randomly labeled with ^{3}H in the diethyl side chain, was obtained in 70 percent ethanol solution with a specific activity of 520 μc/mg from the New England Nuclear Corporation. Upon arrival the compound was subjected to thin-layer chromatography with use of two solvent systems [chloroform, ethanol, and acetic acid (18 : 10 : 2) and trichloromethane and methanol (9 : 1)]. The chromatogram showed three distinct spots in both systems, with approximately 60 percent of the activity corresponding to authentic LSD. The compound was purified on silica gel columns 15 cm long (Quantum Industries) and eluted with methanol. The eluent corresponding to LSD was again subjected to thin-layer chro-