

CHLORINATED SOLVENTS: MARKET INTERACTIONS AND REGULATION*

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Summary

This paper focuses on the five major chlorinated solvents, a class of interrelated chemicals that is currently under regulatory scrutiny for a variety of reasons. It presents historical production data and describes the largest end uses—metal cleaning and dry cleaning. The research explores the opportunities for substitution among the chlorinated solvents. Historical case studies of two of the chlorinated solvents—trichloroethylene, used largely in metal cleaning and perchloroethylene, used heavily in dry cleaning—are examined. These case studies emphasize that regulation without attention to substitution can have unexpected effects. The results of the analysis suggest that because of the complex substitution possibilities, potential future regulation should consider the solvents in concert.

1. Introduction

The Environmental Protection Agency (EPA) is presently considering the regulation of methylene chloride (METH), a widely used industrial chlorinated solvent. The results of recent animal studies suggest that the chemical causes cancer in two species. Although epidemiological studies are negative to date,** methylene chloride's widespread use in a variety of industries may have put thousands of workers and consumers at potential risk of developing cancer. The Food and Drug Administration (FDA) also considered but eventually rejected a ban on the chemical for decaffeinating coffee.***

A significant problem confounds the decision to regulate methylene chloride: many of the chemical's potential substitutes are themselves dangerous, but in different ways. Two of these—CFC-113 and methyl chloroform (TCA)—are suspected of depleting the ozone layer. Trichloroethylene (TCE), another

*Views expressed in this paper are the author's own and are not necessarily shared by the Rand Corporation or its research sponsors.

**We note that many epidemiological studies are frequently not large enough to identify a positive health effect. Negative epidemiological results do not rule out a substance as a carcinogen.

***An environmental organization has filed a lawsuit against the FDA for not banning the chemical.

potential substitute, is a probable human carcinogen and perchloroethylene (PERC), like methylene chloride, has recently shown positive results in animal carcinogenicity studies. The question EPA faces is, if methylene chloride were regulated, would users adopt alternatives that would put them at comparable or greater risk?

The EPA has placed all five of the major chlorinated solvents listed above under regulatory scrutiny, usually for more than one reason. Indeed, as we show below, any regulation on one solvent will inextricably affect the market for one or more of the other solvents. This offers a unique opportunity to consider regulation in concert. In order to do this effectively, however, we must understand the markets which use the solvents, how regulation affects the demand for solvents, and how the threat or fact of regulation alters the behavior of users and producers.

In this paper, we present an overview of the chlorinated solvents with an eye toward pinpointing their interrelationships. In Sections II and III, we present historical production data for each chlorinated solvent and describe two of their major uses. In Section IV, we describe the interrelationships among the solvents beginning with the production process and ending with their use.

In Section V, we discuss the factors that influence the substitution issue. Substitution candidates include other chlorinated solvents, nonchlorinated solvents and other processes for accomplishing the same outcome. As part of this review, we identify certain technical characteristics a solvent must meet, we highlight the health and environmental characteristics of each solvent, and we discuss other regulatory statutes that have influenced their relative demand.

In Section VI, we examine two historical case studies of chemicals under regulatory scrutiny that historically affected the markets for chlorinated solvents. The two cases illustrate the importance of understanding the ways in which the solvents are used and the effect on markets of regulations.

Finally in Section VII, we summarize the factors that influence user and producer response to substitution in the case of the chlorinated solvents.

II. Solvent production

In Table 1, we show annual production for each chlorinated solvent for the period 1964 through 1985. The 1985 data are preliminary and may eventually be revised. Figure 1 pictorially displays the same historical information. The data for PERC, TCE, TCA, and METH come from the International Trade Commission Reports (ITC)*. Because only two producers manufacture CFC-113, production data are not reported to the International Trade Commission. We estimated the values in Table 1 for this solvent using the published literature and data from producers.

TCE production grew steadily through 1970 and declined steadily thereafter.

*These reports were known as The U.S. Tariff Commission reports before 1974.

TABLE 1

Annual production of chlorinated solvents

Year	Annual production (metric tons)				
	TCE	PERC	TCA	METH	CFC-113
1964	168,040	165,892	—	81,466	11,793
1965	197,090	194,752	—	95,631	12,247
1966	217,824	209,867	110,197	121,206	12,701
1967	222,244	241,756	—	118,970	13,608
1968	235,480	288,704	135,808	137,271	14,515
1969	270,713	288,145	147,105	166,017	17,237
1970	277,044	320,643	166,164	182,430	18,597
1971	233,526	319,668	169,914	181,987	19,051
1972	193,541	333,035	199,890	213,767	22,226
1973	204,889	320,154	248,747	235,951	29,484
1974	176,052	333,135	268,360	276,157	31,298
1975	132,773	308,053	208,091	225,489	28,576
1976	143,107	303,422	286,332	243,910	31,298
1977	134,945	278,563	287,960	216,752	36,741
1978	135,618	329,062	292,329	258,592	39,009
1979	144,892	350,640	324,925	287,236	49,895
1980	120,876	347,130	314,008	255,800	57,153
1981	117,109	313,348	278,503	268,546	57,153
1982	—	265,247	269,972	241,430	57,153
1983	—	248,096	265,987	264,880	57,153
1984	—	259,978	305,966	275,209	68,039
1985	—	223,757	268,497	263,378	73,190

Source: U.S. Tariff Commission Reports (1964–1973) for TCE, PERC, TCA, and METH [1]; U.S. International Trade Commission Reports (1974–1985) for TCE, PERC, TCA, and METH [2]; Palmer et al. and authors' estimates for CFC-113 [3].

The events that led to this decline are detailed below. In later years – 1982 through 1985 – production data for TCE were not published by the ITC since all but two producers had closed their plants by then.

The PERC production data show continued growth through the mid 1970s, a slight dip, and strong growth again through about 1980. The significant decline in recent years is a result of several factors we discuss later.

TCA production levels increased over the 20 year period, with a decline in 1982/1983 because of the recession. Production of TCA is presently higher than for all other solvents, illustrating its technical diversity.

METH production exhibited strong growth in the early years and sustaining levels from the mid-1970s onward. As mentioned earlier, the solvent is currently under regulatory scrutiny by EPA's Office of Toxic Substances.

CFC-113 production is lower than that of any other solvent in Table 1.

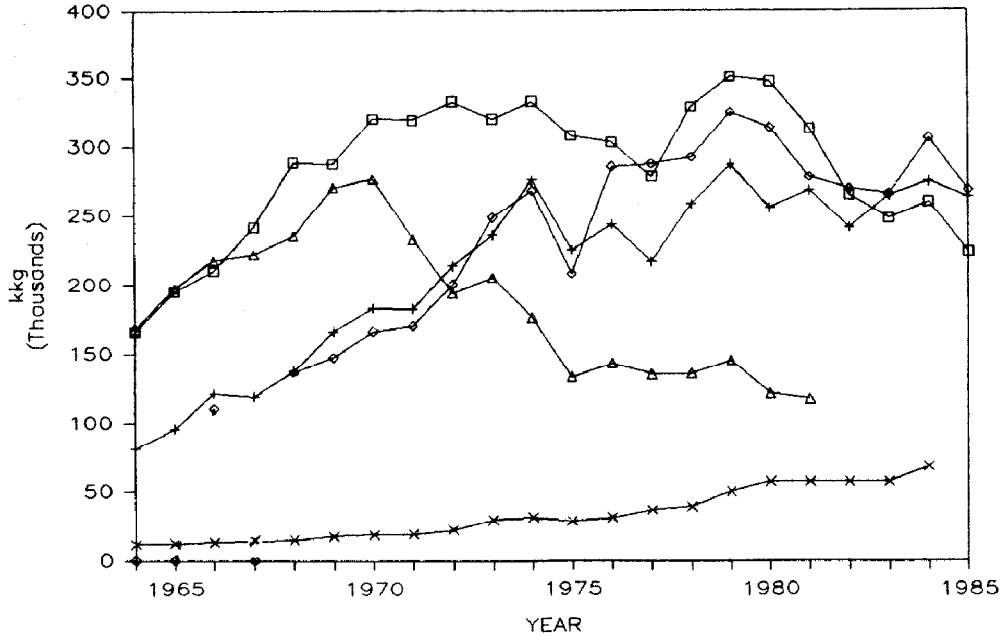


Fig. 1. Annual production of chlorinated solvents: □, PERC; +, METH; ◇, TCA; △, TCE; and ×, CF-113.

Nevertheless, its growth in the last decade has been significant and has been much greater than that of the other solvents.

Production of at least four of the five solvents declined in 1985. Because of the strong dollar in that year, imports increased and exports decreased significantly. It is notable that the lower production levels reflect this trend and that demand for the solvents in the U.S. did not necessarily decline. Indeed, it should be noted that with one exception, in the balance of this paper, we consider U.S. production as a proxy for U.S. demand.*

III. Solvent use

Each of the solvents finds use in a variety of diverse applications. Two of the most interesting – those we focus on here – are metal cleaning and dry cleaning. Below, we discuss each in turn.

Metal cleaning

The term metal cleaning is used to describe activities in a range of sectors including manufacturing, maintenance, and repair. Such activities can be per-

*We are presently collecting import/export data for as much of the historical period as possible. The demand data will be published in a forthcoming document.

TABLE 2

Chlorinated solvent production for cleaning applications - 1985

Solvent	Vapor degreasing		Cold cleaning	
	Percentage of total production	Amount (thousand metric tons)	Percentage of total production	Amount (thousand metric tons)
TCE ^a	53	43	27	22
PERC ^a	7	16	3	7
TCA ^b	28	75	41	110
METH ^c	11	29	4	11
CFC-113 ^d	52	38	20	15
Total	NA	201	NA	165

Source: Table 1; Palmer et al. [3]; CMR (Jan. 27, 1986) [4]; CMR (Feb. 3, 1986) [5]; CMR (Jan. 20, 1986) [6]; CMR (Feb. 10, 1986) [7]; Mooz et al. [8].

NA is not applicable.

^aAssumes one-third of metal cleaning use in CMR (Jan. 27, 1986) [4] and CMR (Feb. 3, 1986) [5] is for cold cleaning and the balance is for vapor degreasing.

^bVapor degreasing use includes vapor degreasing and electronics categories in CMR (Jan. 20, 1986) [6].

^cAssumes one-half of metal cleaning in CMR (Feb. 10, 1986) [7] is for cold cleaning and one-half is for vapor degreasing. Assumes electronics use is vapor degreasing.

^dValues for cold cleaning include liquid phase cleaning and drying percentages given in Palmer et al. [3] and Mooz et al. [8] after adjusting for exports at 7 percent of total estimated CFC-113 production.

formed in small repair shops with only a few employees or large aerospace firms with thousands of employees. Because of the great variability in users, it is not possible to pinpoint one characteristic profile.

Metal cleaning operations can be classified as either cold cleaning or vapor degreasing. In cold cleaning, the solvent generally remains at room temperature or slightly above - but always well below its boiling point. Cold cleaning can involve dipping parts in degreasers with spray attachments or ultrasonic action, or simply wiping parts with a solvent-laden cloth.

In vapor degreasing, the solvent is heated to its boiling point in a tank. The parts are moved through the solvent vapors which condense on the part removing the contaminants. Degreasers are of two types: open top for batch work and conveyerized with automatic feed for continuous cleaning operations.

Table 2 summarizes our estimates of the production of each solvent currently devoted to vapor degreasing and cold cleaning applications. The first and third columns show the percentage of total solvent production that went toward vapor degreasing and cold cleaning, respectively; the second and fourth columns give the amount this implies based on 1985 production figures in Table

TABLE 3

Chlorinated solvent production for dry cleaning - 1985

Solvent	Percentage of total production	Amount (thousand metric tons)
PERC	53	119
CFC-113	3	2
Total	NA	121

Source: Table 1; CMR (Feb. 3, 1986) [5]; Palmer et al. [3] and Mooz et al. [8] after adjusting for exports at 7 percent of CFC-113 production.

1 for all solvents except TCE.* For that solvent, because data on production for 1982 through 1985 are not published, we used the 1985 total demand value given in CMR of January 27, 1986 [4].

Dry cleaning

The dry cleaning process is similar to the more familiar laundering process, but solvent is used instead of water. Clothing and solvent are loaded into the washer and agitated. The clothing is then spun to extract the solvent which is filtered and distilled to remove contaminants. The clothing is tumbled dry and the solvent is either condensed and recovered or vented to the atmosphere. In Table 3, we present our estimate of the percentage of total production and the amount of PERC and CFC-113 presently used in dry cleaning applications. Note that PERC is clearly the most widely used solvent for this purpose with CFC-113 - which is much more expensive - used only for special cases.

Other applications

All five of the solvents find use in a range of other applications. Such uses include intermediate and chemical processing applications, grain fumigation, textile processing, adhesives, aerosols, coatings, paint removal, and foam blowing.

IV. Solvent interrelationships

In Fig. 2, we depict the interactions among the five solvents from the production process through their use.

Four of the five solvents are produced from ethylene dichloride (EDC). As an interim step in the production of TCA, vinyl chloride (VC) is produced. In some plants, PERC and TCE are each produced as a single product; in other

*These values will probably underestimate the amount of each solvent used in cold cleaning and vapor degreasing because the strong dollar in 1985 caused imports to exceed exports by a great deal. For our purposes, however, such a breakdown is in the correct range.

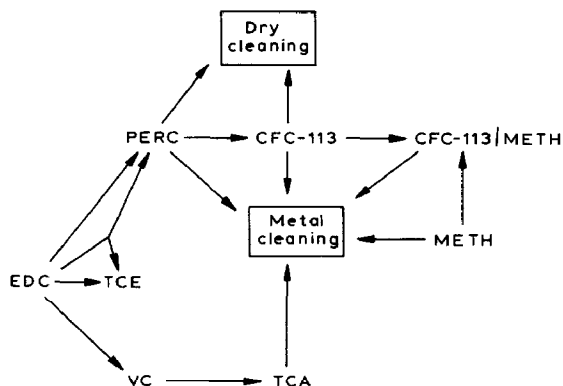


Fig. 2. Chlorinated solvent interactions.

plants, they are co-produced. PERC is used as a precursor chemical in the production of CFC-113. The production process for METH employs a one-carbon precursor chemical – methane or methanol.

As indicated in Fig. 2 and Tables 2 and 3, all five solvents are used in metal cleaning and two – CFC-113 and its precursor chemical, PERC – are used in dry cleaning.

The interactions specified here emphasize the dependence of each of the solvents on the others. If the government regulates one solvent, PERC for instance, it would affect virtually all of the other solvents. Users in the metal cleaning industry would substitute other solvents. Some dry cleaners would substitute CFC-113. In this circumstance, although dry cleaners would use less PERC, its use in producing the additional CFC-113 would somewhat offset the decrease. On the one hand, producers who coproduce TCE and PERC would have to alter their processes to accommodate the lower PERC requirement. On the other hand, if users substituted TCE for PERC in metal cleaning, producers could continue as before. If users substituted TCA for PERC in some metal cleaning uses, the EDC requirement would change slightly.* If users substituted METH for PERC, it would reduce the requirement for a two-carbon feedstock and increase the requirement for a one-carbon feedstock.

This example illustrates the complexity interactions among the solvents. Regulation must address the solvents together and incorporate the effects of their physical interrelationships into the expected outcome.

V. Substitution

No systematic methodology captures the dynamics of substitution among the chlorinated solvents. Many factors should and do enter into an analysis of

*More EDC is required to produce one pound of PERC than to produce one pound of TCA.

TABLE 4

Selected properties of chlorinated solvents

Solvent	Boiling point (°F)	Energy to vaporize solvent (btu/gal)	Solubility parameter	Kauri Butanol number	Wetting index	Evaporation rate ^a	Vapor pressure
TCE	189	1579	9.3	130	87	69	86.7
PERC	252	1723	9.7	90	57	27	120.8
TCA	165	1383	8.4	124	65	139	74.1
METH	105	1654	9.5	136	108	147	40.7
CFC-113	118	943	7.2	31	126	280	47.6

Sources: Mooz et al. [8]; DuPont [9]; Chemical Engineer's Handbook [10].

^aRelative to carbon tetrachloride.

substitution but no straightforward method can prescribe how analysis should evaluate and combine these factors. To give a flavor of the complexity, we consider several of these factors – technical suitability, health and environmental concerns, the impact of various regulatory statutes, and cost. Indeed, these factors interact with one another in ways that modify the results of separate analyses. For convenience, however, we treat each in turn.

Technical suitability

Two classes of potential substitutes must be considered. The first is the other chlorinated solvents; the second is non-chlorinated solvent substitutes and alternative processes.

Table 4 presents a number of selected properties of the five chlorinated solvents. Each of these properties describes a dimension important to vapor degreasing operations,* an application that accounts for a reasonable share of the use of all five solvents. As discussed earlier, in vapor degreasing the solvent is heated to its boiling point to create a vapor zone through which the parts to be cleaned are drawn. Cleaning with solvents like PERC and TCE with high boiling points requires more heat. Vaporizing the solvent requires additional energy. Hence those solvents with higher heats of vaporization like PERC and METH require greater energy expenditure.

The solubility parameter and Kauri Butanol number shown in Table 4 give an indication of the solvent power. The lower these values are, the milder the solvent. TCE and METH are strong solvents, whereas CFC-113 is very mild.

The wetting index, shown in the fifth column of Table 4 reflects the ability of the solvent to penetrate blind spaces in a part and float off the debris. The higher the index, the better the solvent accomplishes these ends. CFC-113 offers an advantage in this respect with METH not far behind.

*Other factors which we do not list include compatibility with plastics, miscibility, and solubility.

The sixth column shows the evaporation rate of each solvent. This characteristic is important in assembly line setups where evaporation must occur quickly before the part goes on to the next step in the operation. The higher the evaporation rate, the more quickly the solvent leaves the part. The vapor pressure of each solvent is shown in the seventh column of Table 4.

The data of Table 4 illustrate that a solvent like CFC-113 would likely be most appropriate for defluxing printed circuit boards. The components are frequently made of delicate materials and CFC-113's mildness would not irritate or swell the boards. Its high wetting index would make it ideal for penetrating crevices created by the components on the board. Furthermore, its low boiling point and heat of vaporization would require little energy.

On the other hand, gross cleaning operations like degreasing metal parts might be accomplished best with TCE. It is a strong solvent as indicated by its high solubility parameter and Kauri Butanol number. This signals that persistent contaminants could be removed without the concern that delicate parts would be damaged. It also has a high wetting index. Although it has a fairly high boiling point, the energy required to vaporize it is reasonably low.

Other technical factors influence the choice of solvent. For instance, TCE and TCA must be combined with a stabilizer additive in many applications to prevent decomposition. Particularly in cleaning applications, the chlorinated solvents are commonly combined with other chemicals to form azeotropes (constant boiling mixture) or blends. In the electronics industry, popular combinations include CFC-113/alcohol or TCA/alcohol mixtures. This facilitates the removal of polar contaminants which are more soluble in alcohol than in the chlorinated solvent. Another mixture, an azeotrope composed of half CFC-113 and half methylene chloride is a somewhat stronger solvent than CFC-113 alone.

Another technical factor that influences the choice of solvent is its compatibility with recovery techniques like carbon absorption for vapors and distillation for waste. Water-soluble components like alcohol and many stabilizers can be removed in the recovery process and a method of analyzing and reconstituting the mixture must be devised.

All the chlorinated solvents are used to some extent in cold cleaning or wiping applications. Because these are generally gross cleaning uses, the stronger solvents like TCE are generally preferred. In such cases, the boiling point and energy to vaporize are not of concern.

As discussed earlier, in dry cleaning applications the most widely used solvent is PERC, although a small amount of TCE is used in fabric scouring, and some TCA is used in textile processing. CFC-113 is also used in dry cleaning to some extent - especially for speciality items like suede and leather. TCE and TCA are not appropriate solvents for industrial and commercial dry cleaning operations because of their instability without stabilizer additives. METH

TABLE 5

Health and environmental characteristics of the chlorinated solvents

Solvent	TLV (ppm)	Carcinogenicity	Smog	Potential ozone layer depletion	Hazardous air pollutant
TCE	100 ^a	Positive	Yes	No	Intent to list
PERC	100 ^a	Positive	Yes	No	Intent to list
TCA	350	In progress	No	Yes	—
METH	500	Positive	No	No	—
CFC-113	1000	Negative	No	Yes	—

Source: ACGIH [13]; Fed. Reg. [14,15]; Quinn et al. [16]; and NTP [17].

^aThe American Conference of Governmental Industrial Hygienists (ACGIH) has recommended that TLVs be lowered to 50 ppm.

is also inappropriate because of the inhibitors added to it to prevent decomposition.

There are a variety of technically suitable substitutes to the chlorinated solvents. In general, each use must be evaluated separately. In electronics applications where CFC-113 and TCA based solvents are presently used, deionized water systems could be substituted. A disadvantage of water, however, is that it may pose technical problems with further miniaturization of printed circuit boards [11].

Alternatives to the chlorinated solvents in metal cleaning applications include aqueous systems, emulsion cleaning and abrasive blasting. Organic solvents of various classes – aliphatic, aromatic and oxygenated – are also potential substitutes [12]. The degree of substitutability depends intimately on the specific application. For instance, organic solvents cannot be used in enclosed conveyorized systems because they could pose a potential threat of explosion. Neither can such solvents be used in vapor degreasers because of their flammability.

In dry cleaning, the alternatives to PERC and CFC-113 are petroleum solvents and water/detergent cleaning. The disadvantage of petroleum solvents is that fire codes in most areas of the country prevent their use. Nevertheless, these solvents are used today and technically could replace PERC. In certain industrial cleaning operations, the goods might be laundered instead of dry cleaned.

Health and environmental effects

In Table 5, we summarize and compare some important characteristics of the chlorinated solvents.

The first column of the table gives the threshold limit value or TLV of each chemical. It is defined as the maximum allowable time-weighted average concentration to which a human may be exposed over an eight-hour working day,

40 hour work week. The higher the TLV, the higher the allowable level of exposure. CFC-113, for instance, has a TLV of 1000 ppm, the highest level allowed. PERC and TCE, on the other hand, have very low TLVs.

The second column in Table 5 indicates whether the solvent has been found carcinogenic in animals. TCE is classified as a probable human carcinogen based on several positive mouse inhalation studies and one marginally positive rat inhalation study [14].

PERC was traditionally classified as a possible human carcinogen. A new inhalation study showed an increased incidence of liver tumors in mice and elevated levels of cell leukemia and kidney tumors in rats. Since earlier mice studies were also positive, the positive finding for rats in particular, is likely to lead to PERC's reclassification as a probable human carcinogen [15].

TCA is presently being tested for carcinogenicity under the National Toxicology Program [17]. It currently falls under the category of chemicals that cannot be classified according to their carcinogenic potential for humans [18].

A recent study performed by the NTP indicates that METH is carcinogenic in both mice and rats. An increased incidence of mammary gland tumors was observed in rats and an increased incident of lung and liver tumors was observed in mice [17].

A recent rat inhalation study performed by Haskell Laboratory on CFC-113 indicated that the solvent is not carcinogenic [18].

The third column of Table 5 indicates whether the solvent forms precursors that lead to photochemical smog (ozone) formation in the lower atmosphere. All chemicals are considered to contribute to ozone in the troposphere unless specifically exempted. TCE and PERC are not exempted; TCA, METH and CFC-113 are [19]. PERCs half-life in the atmosphere is of the order of months whereas that of TCE is shorter – a matter of days.

The fourth column indicates whether the chemical potentially contributes to ozone layer depletion in the upper atmosphere or stratosphere. Because CFC-113 contains no hydrogen, it is not subject to attack by the hydroxyl radical in the lower atmosphere. It therefore survives intact until it reaches the stratosphere where ultraviolet light leads to decomposition. The liberated chlorine can react catalytically with the ozone. CFC-113 is potentially a strong ozone depleter because of its long atmospheric lifetime – around 86 years. TCA has a shorter atmospheric lifetime – about eight years, but enough of the chemical survives to be transported to the stratosphere [16,20]. TCE, PERC and METH have much shorter atmospheric lifetimes so that they do not pose a potential threat to the ozone layer.

Non-chlorinated solvent substitutes include organic hydrocarbons, and petroleum solvents. These substances are virtually all flammable, and most are precursors to photochemical smog.

Regulatory statutes

The chlorinated solvents and many of their potential substitutes are regulated under various statutes with oversight by a number of government agencies. In what follows, we briefly mention the most important regulations in terms of the general environment. We exclude oversight by the Occupational Safety and Health Administration (OSHA) which is responsible for workplace regulation.

Volatile organic compounds

In 1977, EPA announced its "recommended policy on the control of volatile organic compounds (VOCs)". Periodically thereafter, the agency issued lists of organic compounds that are negligibly photoreactive and thus exempt from regulation to attain the national ambient air quality standards under State Implementation Plans (SIPs).

Exempted VOCs include methane, ethane, METH, TCA, and eight CFCs. In 1983, EPA issued a notice to propose that PERC be exempted as well. The proposal was never made, however, and PERC is therefore considered photochemically reactive along with TCE [19].

A number of states have regulations designed to reduce emissions of photochemically reactive substances. They commonly require an 85 percent reduction. In the case of PERC, for instance, such reductions are required for dry cleaners, solvent metal cleaners, and for fugitive emissions from other sources. Some states adopt these standards only for nonattainment areas – areas that have not achieved the ambient air quality standards for ozone – whereas others adopt them statewide.

The photochemical reactivity of PERC and TCE has significantly influenced their historical and current use and emissions patterns. We discuss the consequences of this designation later.

Section 112 of the clean air act

Under Section 112 of the Clean Air Act, EPA can set National Emission Standards for Hazardous Air Pollutants (NESHAP). Hazardous air pollutants are defined as air pollutants that "contribute to mortality or serious irreversible, or incapacitating reversible, illness" [14]. The list presently includes the carcinogens asbestos, beryllium, mercury, and vinyl chloride.

In December of 1985, EPA issued a Notice of intent to list TCE and PERC under Section 112 apparently because of the recent positive animal carcinogenicity tests on both [14,15]. The agency intended to solicit information on the use, emissions, and health effects of the two chlorinated solvents.

Toxic substances control act (TSCA)

Largely in response to the positive carcinogenicity test on METH, it has been listed under Section 4f of TSCA which designates the chemical for prior-

ity review. This listing provides 180 days for EPA to decide whether or not the chemical poses a significant risk.

Clean water act

Four of the chlorinated solvents – TCE, PERC, TCA, and METH – are designated under the Clean Water Act. This means that EPA is required to set water quality standards for these substances.

Food and drug administration (FDA)

The FDA briefly considered and rejected a regulation preventing the use of METH for decaffeination of coffee and spices. The Delaney Clause requires FDA to ban all food additives that are animal carcinogens. In this case, the FDA designated METH a decaffeinating agent rather than a food additive. A lawsuit challenging this interpretation has been filed by citizens and environmental groups.

Comprehensive environmental response and compensation act (CERCLA)

All five chlorinated solvents considered here are listed as hazardous substances under 101 (14) of CERCLA or “Superfund”. A largely collateral effect of superfund is that users may reduce the volume or eliminate altogether the waste they presently send to hazardous waste disposal sites because of potential future liability. As described below, a host of changes may occur in response to the hazardous waste legislation of the last decade.

Resource conservation and recovery act (RCRA)

All five chlorinated solvents are subject to the manifest system set up under RCRA. In 1984, Congress passed sweeping amendments to RCRA specifying a ban on land disposal of virtually all hazardous substances within the following six years. The first set of substances that will be banned from land disposal on November 8, 1986 are dioxins and solvents [21].

On January 14 of 1986, EPA announced that it would exempt certain users if they petitioned and would extend the deadline for solid sludges and dilute wastewater containing solvents for the full two-year period allowed by Congress [22]. The reason given for the delay was that alternative technologies – treatment methods for dilute aqueous streams and rotary kilns for solid sludges – were not yet widely available.

When this amendment goes into effect for users over the period November of 1986 through November of 1988, it will change the fundamental structure of the solvents market. Producers and users will seek alternative methods of dealing with the solvents over their life cycle. Users will attempt to reduce emissions and waste losses in-plant; substitution to alternative processes and substances exempt from the ban or more easily conserved will occur wherever

TABLE 6

Current prices of chlorinated solvents

Solvent	Price (cents/pound)
TCE	38.5
PERC	28
TCA	42 ^a
METH	26
CFC-113	89

Source: CMR (February 10, 1986) [7], CMR (January 20, 1986) [6], CMR (February 3, 1986) [5] and CMR (January 27, 1986) [4].

^aAverage of reported range.

possible; the demand for external reclamation services will increase so users can avoid the disposal problem; and demand for incineration will increase.

Cost of substitution

The current bulk prices of the chlorinated solvents are shown in Table 6. Unit values based on the sales of TCA and CFC-113 are not reported in the International Trade Commission Reports because there are only two firms who produce the chemicals. We therefore present prices for all five solvents from the Chemical Marketing Reporter.

The values of Table 6 show that the price of CFC-113 is much higher than those of the other solvents. This explains its use in high technology and critical cleaning applications where its special characteristics are required for production of high-value products. Prices of METH and PERC are low; prices of TCE and TCA are somewhat higher.

To some extent, the difference in price of the solvents suggests a difference in cost in their use. For the most part, however, the cost of using a particular solvent depends more heavily on the other factors discussed in this section. In vapor degreasing and cold cleaning applications for instance, the cost of using a particular solvent will be lower if the solvent is compatible with methods of reducing emissions or waste. These techniques minimize total solvent losses and reduce the cost of uses. Solvent users commonly distill used solvent to recover reusable solvent from waste. Solvent blends and solvents that require stabilizers are more expensive to distill than pure solvent. Components and stabilizers are separated from the solvent during the process and the combination must be constituted before it can be reused. Carbon adsorption techniques for recovering solvent vapor emissions can be used more easily and is less costly for TCE than for TCA.

Flammable hydrocarbons or chlorinated solvents with flammable alcohol components are more expensive to use than nonflammable substances. Solvents with low TLVs – like TCE and PERC – require more workplace venti-

lation than solvents with high TLVs. Solvents that contribute to photochemical smog require plant emission control devices. Solvents suspected of carcinogenicity may eventually be more costly to use because of the possibility of future lawsuits.

Another important cost of using a solvent is the cost of disposal. In recent years, such costs have escalated. Furthermore, several waste disposal sites have been closed either because they do not meet new RCRA standards or because they have been found to be leaking. This leaves fewer sites available and raises the cost of disposal. Potential future costs from liability or cleanup can also add to the cost of using a solvent.

VI. Historical case studies

In what follows, we examine two historical case studies involving several of the solvents we are considering here. The dominant theme throughout is that regulation or even regulatory scrutiny of one of the solvents can push users to other solvents that may pose a different, but perhaps, as severe, a threat as the original solvent. These cases emphasize the diverse factors that must be taken into account when regulation is contemplated. A good knowledge of the solvent markets and the historical experience can lead to a much enlightened and comprehensive future regulatory strategy.

Case 1: TCE

For nearly three decades after World War II, TCE was the most widely used solvent for metal cleaning and degreasing. Because of its ubiquity and its mobility, the solvent is frequently found today in ground water aquifers and drinking water wells across much of the country.

Over the last several years TCE was the subject of repeated regulatory scrutiny. In what follows, we examine the response to this scrutiny in two ways. First, we track historical production and link users' declining solvent demand to increasing regulation. Second, we follow production capacity which measures the definitive response of producers to regulation or the threat of regulation.

Accordingly, we refer throughout to the TCE production levels for the period 1964 through 1981 shown in Table 1. In Table 7, we present a record of historical TCE producers and the production capacity held by each.

TCE has an especially rich regulatory history. In 1964, there were five major TCE producers with plants in seven locations. According to the values in Table 7, TCE capacity expanded modestly between 1964 and 1966. The Oil, Paint and Drug Reporter (later known as the Chemical Marketing Reporter) announced that 1965 was a good year for the solvent. "If trichloro is in the strongest position of all (compared with PERC and carbon tetrachloride), it is because of rising aerospace and military demand. The Vietnam War has brought stepped up procurement of it as a degreasing solvent for military

TABLE 7

Historical TCE plant capacity (thousand metric tons)

Producer	Year									
	1964	1966	1969	1972	1975	1978	1981	1983	1985*	1986*
Detrex (Ashtabula, OH)	32	36	45	—	—	—	—	—	—	—
Dow (Freeport, TX)	14	23	91	68	68	54	54	54	54	54
Dow (Plaquemine, LA)	16	18	16	—	—	—	—	—	—	—
DuPont (Niagara Falls, NY)	102	102	125	—	—	—	—	—	—	—
Hooker (Niagara Falls, NY)	20	27	27	—	—	—	—	—	—	—
Hooker (Tacoma, WA)	11	14	14	14	—	—	—	—	—	—
PPG (Barberton, OH)	20	36	—	—	—	—	—	—	—	—
PPG (Lake Charles, LA)	—	—	36	91	91	100	100	100	91	91
Diamond Shamrock (Deer Park, TX)	—	—	27	27	23	23	—	—	—	—
Ethyl (Baton Rouge, LA)	—	—	18	18	18	23	23	—	—	—
Hooker (Taft, LA)	—	—	18	27	18	18	—	—	—	—
Total	215	256	417	245	218	218	177	154	145	145

Note: Capacities are flexible because the equipment is also used to produce PERC.

Source: OP&DR, June 15, 1964 [23]; OP&DR, July 11, 1966 [23]; OP&DR, October 6, 1969 [23]; CMR, November 20, 1972 [4]; CMR, September 22, 1975; CMR, June 26, 1978; CMR, April 6, 1981; CMR, February 14, 1983 [4]; Farhad and Elkin [24].

*Excludes ethyl's 45 million pound/year plant which is on standby (probably forever).

equipment" [25]. Indeed, the values of Table 7 reflect a 19 percent production increase between 1964 and 1966. According to the industry, a capacity expansion was predicted. "Trichloro is limited not only by the shortage of chlorine, but like methylene chloride, capacity for the solvent itself is lagging behind the market's growth" [25].

In 1966, growth remained strong as shown by the production values of Table 1. The industry reported that, "Recent growth has been largely spurred by the war effort....," and "Four producers not now in trichloroethylene, but in other chlorinated solvents are rumored looking at the market" (July 11, 1966 [23]). The values of Table 7 show that at least two new producers – Diamond Shamrock and Ethyl Corporation – did enter the market between 1966 and 1969. Indeed, by 1969, capacity had increased by more than 60 percent over 1966 and there were then seven producers with a total of ten plants.

In 1968, Los Angeles County adopted Rule 66 which limited emissions of TCE [26]. The TCE producers and the Manufacturing Chemists Association (later the Chemical Manufacturers Association or CMA) commissioned a study to be performed by Stanford Research Institute to determine whether the solvent actually contributes to photochemical smog. Early in 1969, SRI "reported preliminary findings which seemed to clear trichloro of any serious role in pollution, but it was felt that the data were not really conclusive, and the study was extended. If the final report is favorable to trichloro, the producers, DOW

among them, will press for a reversal of the Los Angeles County Rule. Orange County and the San Francisco area are expected to take the SRI findings into account in deciding on whether trichloro should be controlled as a pollutant" [27].

The SRI study showed (incorrectly, it was later determined) that TCE did not contribute to photochemical smog. In 1970, the industry reported that "Trichloro also is holding its own in its conflict with what the industry believes to be overzealous antipollution efforts on the West Coast," [28]. Indeed, Table 1 shows that production of TCE continued to increase through 1970.

By 1972, the industry reported that several states had enacted legislation similar to L.A. County's Rule 66. The decline in production shown by the values of Table 1 apparently reflects the slowdown in demand. More important, perhaps, is the significant decrease in capacity – more than 60 percent – shown in Table 7 for the period 1969 to 1972. Out of the 10 plants producing TCE in 1969, only 6 remained by the end of the period.

By 1975, industry conceded "Trichloroethylene is very photoreactive. Federal and local governments have severely restricted use and emissions of TCE in vapor degreasing plants in many areas of the country in order to reduce air pollution" (September 22, 1975 [4]). Another seminal event that signaled the final demise of TCE was a "Memorandum of alert" on TCE issued by the National Cancer Institute (NCI) in April of 1975. Preliminary findings in bioassays of the solvent indicated that it would show carcinogenic activity in mice [29]. The test had been prompted in previous years when EPA reported that TCE and vinyl chloride—a known human carcinogen—were metabolized similarly in humans.

The values of Table 1 illustrate the effect the smog finding and the animal study results had on the production of TCE. From the peak of 277 thousand metric tons in 1970, production declined more than 50 percent, to 133 thousand metric tons in 1975. The capacity data in Table 7 for the period between 1972 and 1975 also show a continuing decline.

In the next decade, TCE never regained its popularity as EPA placed increasingly stringent regulations on emissions of the solvent. Production continued at the lower levels as shown in Table 1. According to Table 7, capacity declined further as all but two producers finally exited the market. In the early 1980s the American Conference of Governmental Industrial Hygienists (ACGIH) recommended that the workplace TLV be lowered to 50 ppm from 100 ppm where it had been for more than 20 years.

As TCE, once the chlorinated solvent in highest demand, was gradually phased out of the market, what took its place? Before the smog issue was resolved in 1969, it was reported that "Opinions in the industry diverge widely on trichlor's future. Some foresee sharp encroachment by 1,1,1-trichloroethane (TCA) as capacity for the latter becomes top heavy. Others believe trichloroethylene will hang on to its existing market," (October 6, 1969 [23]).

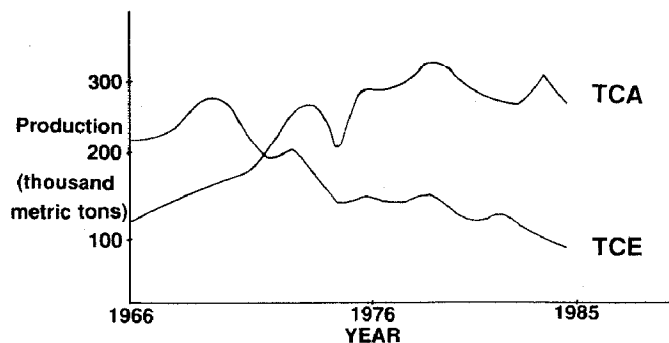


Fig. 3. Historical TCE and TCA production.

In 1977, the industry stated of TCA, "Conversion from trichloroethylene, especially in vapor degreasing will keep growth fairly strong," (January 17, 1977 [6]).

By 1975, the conversion was in full swing. In 1974, the industry reported that "Conversion from trichloroethylene to 1,1,1-trichloroethane to comply with air pollution standards has proceeded rapidly in solvent and degreasing applications," (January 22, 1974 [6]). A few years later, industry reported, "A gradual decline in the use of trichlor now seems inevitable. Substitution of trichlor with such alternative solvents as perchloroethylene and 1,1,1-trichloroethane is being actively pushed by some manufacturers. The pace of substitution may well be accelerated in the next several years, as at least one trichlor market is known to favor a total phasing out of trichlor in favor of alternative chlorinated solvents," (April 6, 1981 [4]). In 1983, industry claimed that "Some substitute solvents like 1,1,1-trichloroethane are said to be replacing trichloroethylene," (February 14, [4] 1983).

In Fig. 3, we show TCE and TCA production for the 20 year period. From these data, it certainly appears on the surface at least, that TCE was largely replaced by TCA. To explore this notion more fully, we show the history of TCA's capacity in Table 8. Comparing the values of Tables 7 and 8, we observe a production capacity decrease of 270 thousand metric tons for TCE from 1969 through 1986. We also observe an increase of about 315 thousand mt of TCA capacity from 1968 through 1986. This suggests that TCA capacity increased to fill the gap left by TCE plants that were closing.

The story of TCE is one of continued decline under increasing regulatory scrutiny. It initially appears that TCA was substituted for TCE largely in metal cleaning applications.* In its remaining uses, TCE must offer a clear technical

*PERC may also have substituted for TCE to a small extent. The production capacity for PERC in 1969 (390 thousand metric tons) was approximately the same as the 1986 capacity (392 thousand metric tons) [30]; 1970; (CMR February 3, 1986 [5]). It is not possible to sort out the offsetting effects of a decline in demand for dry cleaning (see below) and substitution for TCE.

TABLE 8

Historical TCA plant capacity (thousand metric tons)

Producer	Year					
	1968	1971	1974	1977	1982	1986
Dow (Freeport, TX)	91	136	154	204	204 ^a	204 ^a
Ethyl (Baton Rouge, LA)	23	18	23	—	—	—
PPG (Lake Charles, LA)	23	79	79	79	159 ^b	159
Vulcan (Geismar, LA)	—	23	29	29	91	91
Total	137	256	285	312	454	454

Source: OP&DR, March 25, 1968 [31]; OP&DR, April 26, 1971 [31]; CMR, January 22, 1974 [6]; CMR, January 17, 1977 [6]; CMR, September 27, 1982 [6]; CMR, March 28, 1983 [6]; CMR, January 20, 1986 [6].

^aDow has a 136 thousand metric ton per year unit on standby at Plaquemine, Louisiana which came on line in 1978.

^bPPG has a 79 thousand metric ton per year unit on standby at Lake Charles, Louisiana.

advantage since it is costly and inconvenient to use a solvent with a recommended TLV of 50 ppm.

What lessons does the TCE case teach us about substitution and regulation? First, as TCE came under increasing regulatory pressure, production declined as users substituted adequate and reasonably low-cost alternatives where they could. Second, the TCE case is one of steady erosion rather than an abrupt definitive ban. Since no regulation followed the TCE animal carcinogenicity finding in 1974, there remains an expectation that more stringent regulation may occur in the future. This is revealed in the continuing decline in TCE use. Third, the continued scrutiny of TCE for more than 15 years caused all but 2 of the seven producers to close their plants.

Case 2: PERC

In Table 9, we present the historical record of PERC production capacity. This, combined with the production levels of the solvent given in Table 1 allow some insights into the historical PERC market.

The values of Table 1 show that PERC production increased steadily until about 1972, held constant until 1980, and went into a decline thereafter. The capacity figures of Table 9 show a similar trend – an increase in the early years and a decline in capacity after about 1979.

In our analysis here, we wish to focus on the dry cleaning industry. Accordingly, in Table 10, we present the percentage and amount of PERC devoted to four end uses – “dry cleaning”, “industrial metal cleaning”, “chemical intermediate”, and “other”. Instead of using the production totals for 1978 and 1985 in Table 1, we use demand values presented in the Chemical Marketing Reported. These values exclude exports and include imports which increased

TABLE 9

PERC production capacity

Producer	(thousand metric tons)						
	1970	1973	1976	1979	1982	1983	1986
Detrex (Astabula, OH)	11	—	—	—	—	—	—
Diamond Shamrock (Deer Park, TX)	45	75	75	75	75	75	75
Dow (Freeport, TX)	54	54	54	68	68	68	—
Dow (Pittsburg, CA)	9	9	9	18	23	23	23
Dow (Plaquemine, LA)	68	68	68	54	41	41	41
DuPont (Niagara Falls, NY)	27	—	—	—	—	—	—
Ethyl (Baton Rouge, LA)	23	23	45	23	23	—	—
Hooker (Tacoma, WA)	5	—	—	—	—	—	—
Hooker (Taft, LA)	16	23	27	—	—	—	—
PPG (Lake Charles, LA)	32	91	109	91	109	109	91
Stauffer (Louisville, KY)	32	32	—	32	—	—	—
Vulcan (Geismar, LA)	50	68	68	68	68	68	68
Vulcan (Wichita, KS)	18	23	23	23	23	23	23
DuPont (Corpus Christi, TX)	—	—	—	73	73	73	73
Total ^a	390	466	478 ^b	525	503	480	394

Source: OP&DR (Nov. 30, 1970) [30]; CMR (August 13, 1973); CMR (August 9, 1976) [5]; CMR (June 18, 1979) [5]; CMR (March 22, 1982) [5]; CMR (March 14, 1983) [5]; CMR (Feb. 3, 1986) [5].

^aCapacities can vary by as much as 60 percent depending on the relative demand for the coproducts (TCE and carbon tetrachloride).

^bTotal value of 501 thousand metric tons in CMR of August 9, 1976 [5] is incorrect.

TABLE 10

PERC end use allocation

Use	1978		1985	
	Percent ^a use (thousand metric tons)		Percent ^a use (thousand metric tons)	
Dry cleaning and textile processing	64	207	56	151
Chemical intermediate	14	45	29	78
Industrial metal cleaning	16	52	11	30
Other	6	19	4	11
Total	100	323	100	270

Source: Table 1 and CMR (February 3, 1986) [5]; CMR (June 18, 1979) [5].

^aExports at 6 percent and 5 percent of production in 1978 and 1985 respectively have been taken into account.

significantly in 1985. A comparison of the values of Table 1 with those of Table 10 shows that the Chemical Marketing Reporter estimates of imports in 1978 amounted to about 14 thousand metric tons whereas those in 1985 were much higher – 57 thousand mt.* The increased level of imports also explains the difference in the figures of Tables 2 and 3 – which are based on production—and the figures of Table 10 – which are based on estimated demand.

The values of Table 10 show that PERC use in dry cleaning and textile processing declined by 28 percent over the period. Use of the solvent as a chemical intermediate increased by 73 percent. This increase is in the same range as the increase in CFC-113 production of 87 percent in Table 1 for the same period.** Use of PERC in metal cleaning declined by 42 percent over the period. Total PERC demand for the period declined by 16 percent.

What caused the decline in recent years in the amount of PERC used in dry cleaning and metal cleaning? The trend may have started in 1976 when the industry reported, “Domestic dry cleaning is on the decline,” (August 9, 1976 [5]). The reason became obvious in 1979 when the industry explained, “The increasing popularity of wool blends, silks and other clothing fabrics that must be dry cleaned has shored up demand that had been undercut by wash-and-wear wardrobes”. The same source indicated that, “More efficient dry-cleaning machines reduce demand,” (June 18, 1979 [5]).

In 1978 and 1979, OSHA developed a new carcinogen classification scheme. Around the same time the Consumer Product Safety Commission (CPSC) developed its own carcinogen policy. The first chemical to be classified by CPSC was PERC. Indeed, in 1979, the industry reported that, “CPSC has clouded PERC’s future by branding it a carcinogen. Growth is tied otherwise to population trends. Petroleum cleaning solvents will not replace PERC because of their flammability. Government actions, if they came would most alter PERC’s future,” (June 18, 1979 [5]). Sometime later, CPSC withdrew its proposal to classify PERC as a carcinogen. The action, however, may have had an effect on the market.

By 1982, PERC production had declined significantly (see Table 1). One industry source claims that there are two reasons for the long-term decline. First, synthetic fibers replaced natural fibers in the 1970s to some extent in this country. Dry cleaning, for these garments, was no longer necessary. Second, because of PERC’s nonexempt status in terms of photochemical smog, dry cleaning (and metal cleaning) equipment has become more efficient and

*This assumes that exports in 1978 and 1985 amounted to 6 percent and 5 percent of production respectively.

**Recall that PERC is used to produce CFC-113. Because of the strong 1985 dollar, we would expect imports of CFC-113 to be greater than in 1978. This imported CFC-113 would not require PERC as a precursor chemical. Since our CFC-113 “production” estimates actually reflect demand, we would expect CFC-113 demand which includes these imports to increase more than PERC demand for CFC-113 production.

solvent losses have been reduced considerably. Thus, demand for virgin PERC has declined.

The Chemical Marketing Reporter seems to verify the second reason. In 1982 it claimed that, "More efficient dry-cleaning machinery, stewardship programs, and recycling steadily reduced demand for the material (PERC)," (March 22, 1982 [5]). In 1986, this theme was reiterated. "Greater recycling and less solvent emissions from dry cleaning equipment and metal cleaning machinery have gradually reduced PERC demand in these sectors. Demand for PERC in the dry cleaning and metal cleaning industry will continue to decline slowly, but gains in the F-113 businesses will largely offset this loss barring further restrictions on PERC's use," (February 3, [5] 1986).

In general terms, metal cleaning equipment for all solvents including PERC has been tightened up, at least partly because of the increased regulatory scrutiny of the chlorinated solvents. In dry cleaning specifically, one reliable industry source attributes the more conservative measures partly to cost considerations but also to more stringent environmental regulations. He cited the smog regulations which have led to additional controls. He maintained that the nonexempt status of PERC under Section 112 of the Clean Air Act classifying it a hazardous air pollutant (see Section on Substitution) and the recent positive animal carcinogenicity tests were more influential. He claims that dry cleaners are not only nervous about employee lawsuits from exposure to a potential carcinogen but also are concerned that there could be lawsuits from people living in the neighborhood if they later developed cancer.

These comments suggest that once a substance becomes a suspected carcinogen, the market can react strongly. It is not clear whether the reaction occurs because the industry believes that regulation or lawsuits will follow or because they do not want their employees exposed to suspect carcinogens.

Another industry source indicates that dry cleaners are responding to the RCRA regulations by adopting a variety of more conservative methods. Most of these firms are small quantity hazardous waste generators* who have recently become subject to RCRA reporting requirements. One reclamation firm has contracts to reclaim the waste generated by 15,000 of the 25,000 commercial and industrial dry cleaners.** The PERC is reclaimed at one of seven reclamation centers owned by the firm. The cost to the dry cleaner is substantially less than the cost of land disposal*** or incineration. The industry source describes this reclamation network as a life saver for the dry cleaning industry. Indeed, since there is little enforcement of small quantity generators, the recla-

*Such firms generate between 100 and 1,000 kg of hazardous waste each month.

**There is one smaller reclaimer who offers this service in California.

***Land disposal sites are closing rapidly as more of them are found to be leaking. There may be few or no sites in the area of the generator. Transportation and logistics costs can raise the cost of land disposal significantly.

mation firm has set up a structure for brining dry cleaners under the rubric of RCRA at a reasonable cost.

The case of PERC is interesting because it illustrates that a market can decline for a host of reasons rather than because of one significant event. Production and production capacity have decreased gradually in the 1980s in response to tighter regulations on air and water emissions and hazardous waste.

VII. Conclusions

The two case studies presented here highlight the interactions that can occur among members of the class of chlorinated solvents when one of them is regulated or placed under regulatory scrutiny. Such interactions occur in the production, use, and disposal of the solvents. These interrelationships can lead to unexpected and unacceptable consequences and market dislocations when one of the members of the class is regulated.

There are three fundamental factors that policymakers should take into account when considering future regulatory action on one or more of the solvents. First, the policymaker must develop a good understanding of the technical characteristics of each solvent. Technical knowledge helps in anticipating the consequences of regulation in a particular use. In the early 1970s, for instance, users faced with increasing regulation of TCE largely replaced it with TCA, apparently its closest substitute.

Second, the policymaker must take into account the other environmental and health effects of the solvents when considering whether or not to regulate. The replacement of TCE, a probable human carcinogen – by TCA, a potential ozone depleter – occurred in the 1970s. Such outcomes should be anticipated and may be deemed undesirable in the future.

Third, we must remain aware of the fact that not only regulation but simply the threat of regulation may cause large dislocations in the markets for chlorinated solvents. The case of PERC illustrates this point.

The chlorinated solvents are an extremely useful class of chemicals for emphasizing the difficulties of regulating toxic substances sensibly. Each of them poses a variety of health and environmental threats and further regulation will almost certainly occur in the future. A good knowledge of the solvent markets and an awareness of their interrelationships from production through disposal will help policymakers to choose intelligent regulatory strategies.

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