The Dark Side of Petkim

GREENPEACE

The Dark Side of Petkim: PVC

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Table of Contents :

1. INTRODUCTION

Over the past three years, Greenpeace has carried out a number of investigations of the wastes generated and contamination caused by Petkim's Aliağa plant, one of Turkey's main PVC producers. This report summarises much of the research and explains the processes and problems behind the product that many call "the poison plastic".

The chlorine industry manufactures chlorine primarily to combine with petrochemicals to produce organochlorine products such as solvents, pesticides, plastics (especially PVC) and many other chemicals. A much smaller proportion of the chlorine gas is sold outside the chemical industry, primarily as bleach in the production of paper and for drinking water disinfection.

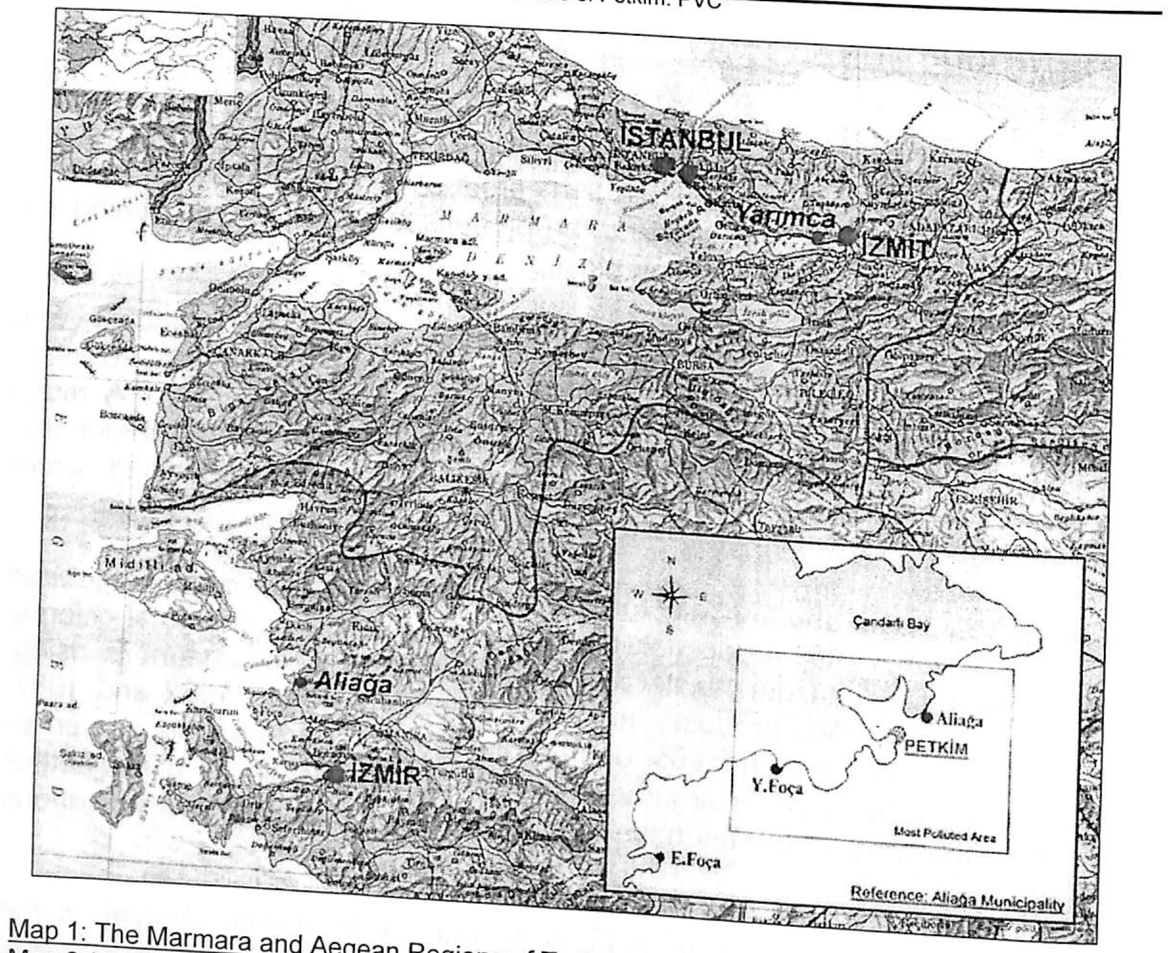
On a global basis, the PVC sector is the largest single user of manufactured chlorine. Global PVC production consumed 30% of the world's total chlorine output in 1990 (van der Naald & Thorpe 1998) and this amount is rising. Consumption of PVC products in Turkey doubled between 1982 and 1987. Since the beginning of the '90s, demand for PVC products has increased so much that many more environment friendly products such as glass bottles and wooden window frames have started to be replaced with this poisonous plastic.

The representative of the Petrochemical Industry in Turkey, Petkim, is the sole PVC, and the major chlorine, producer. The aim of this study is to reveal the toxic substances generated as a result of the manufacturing processes employed at Petkim and their effects on the environment and humans. It also aims to show how chlorine and chlorinated products such as PVC threatens our health while they are promoted by their producers as improving our lives.

2. REPRESENTATIVE OF PETROCHEMICAL INDUSTRY IN TURKEY

Petkim Petrochemical Co. was founded on April 3, 1965 for the purpose of establishing and developing the petrochemical industry in Turkey. The first five plants of the first Petrochemical Complex in Yarımca/İzmit were put on stream in 1970.

In consideration of the continuous growth of domestic demand for petrochemicals at the Turkish market Petkim expanded the plant capacities of Yarımca complex, added new units and decided to set up the second petrochemical complex in Aliağa/İzmir.



Map 1: The Marmara and Aegean Regions of Turkey.
Map 2 (right bottom corner): The Aliağa Area.

Petkim Tire Manufacturing and Trade Co. was also founded in Kırşehir under the leadership of Petkim. The status of the company has been altered to PETKİM PETROCHEMICAL HOLDING CO. as of April 25, 1988.

Today, Petkim produces about 50 petrochemical substances used as raw materials by industries such as plastics, textile, rubber, automotive and electronics manufacture at the Yarımca and Aliağa complexes. Total production capacity has now reached 2.9 million tons per year.

Manufacturing synthetic materials is a complex process. Many different chemical reaction stages are employed in order to turn naturally occurring raw materials into the final products sold to other industrial processors or to the public. Consequently, large integrated plants like Petkim were set up to allow its owners to make use of the byproducts from one process to manufacture another. In theory it is an efficient system but if the wrong products or processes are chosen, then the potential for severe environmental problems arises.

The primary feedstock at Petkim is oil. At Aliağa, 1,500,000 tonnes of naphtha per year are processed to produce petrol, solvents and plastics. The environmental problems resulting from petrol are not restricted to its toxicity and will not be discussed further here. Some of the plastics produced have comparatively low environmental impact (eg polyethylene and polypropylene) or are readily recyclable (eg PET). All these compounds are based almost totally on the elements of carbon, hydrogen and oxygen.

At the same time, another sector of the plant concentrated on the production of chlorine and chlorinated materials, utilising some of the products of the hydrocarbon sector of the plant as a feedstock. The chlorine and chlorinated materials sector produces a range of toxic and persistent chemicals, both as products and byproducts The primary use for chlorine at Aliağa is to make PVC.

Almost every stage of the PVC lifecycle creates pollution problems. At the beginning of the process, mercury is used to help make chlorine. This is then converted to ethylene chloride and then vinyl chloride- both toxic hazardous chemicals- in a process that generates dioxins and many other pollutants. Vinyl chloride is polymerised to make PVC. PVC is a poor plastic which cannot be used to make products without a variety of additives. Many of these are hazardous, and can leach out of the product during its use. Some products have been withdrawn from sale in recent years in North America and Europe because of fears about their potential health effects, especially on children. Even at the end of a PVC product's useful life, it may still pose environmental problems. PVC is very difficult to recycle- in practice it almost never happens. Finally, landfilling or incinerating PVC can release still more toxic chemicals.

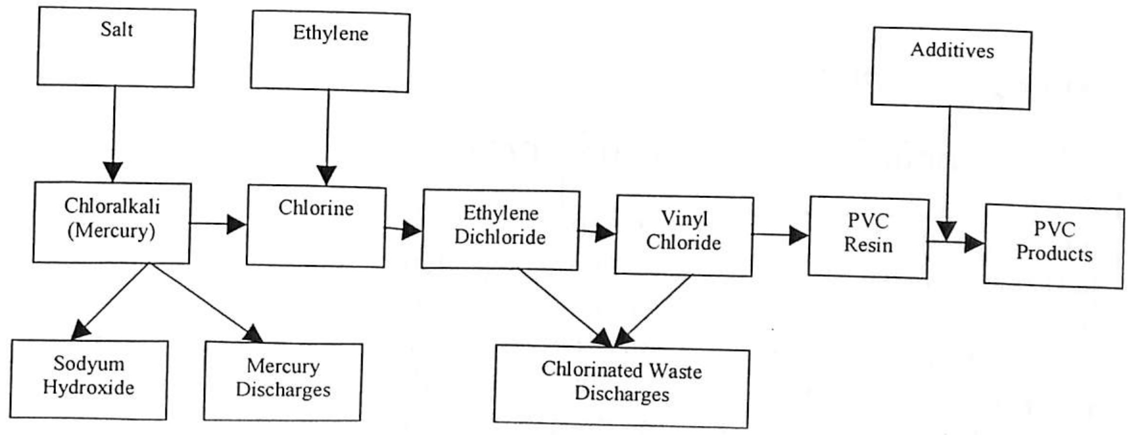


FIGURE 1: Flow chart of PVC production

2.1 Yarımca Complex

Yarımca complex is located in Yarımca/İzmit on the Marmara Sea 80 km from İstanbul. İzmit became an industrial center in the second half of the 1960s. There are many kinds of industries located here, with products such as textiles, chemicals, pulp and paper, fertilisers, petrochemicals, cars, chlorine and caustic soda. Most are located in Dilovası, Yarımca and in the city of İzmit itself.

İzmit Bay is a relatively long, narrow and rather shallow bay located on the east side of the Marmara Sea. Being situated not far from the Bosphorous and Istanbul, it used to be a site for leisurely recreation and fishing. The bay has now become renowned for the dynamic development of industry while the fishing fleet has diminished (Okay *et al.* 1996).

The following factories at the Yarımca Complex started operating in 1970: ethylene, low density polyethylene, chlor-alkali, VCM and PVC. Between 1972 and 1976 six other factories producing different petrochemical products were set up.

While Yarımca complex had the capacity and the technology to meet the domestic demand in the period it was established, demand soon exceeded its production capacity. By the 1980s, the complex was hampered by its limited capacity and outdated technology. According to the feasibility studies, the life for factories are stated to be 10 years and 15 years for the auxiliary units. Compared to modern processes, in 1993, the Yarımca complex consumed 25-50% more energy, more raw material and generated more byproducts (Petkim 1994). Consequently, starting from 1991, units that were losing money were closed down. EDC and VCM plants operate from time to time according to the prices and the availability. Privatisation plans are now preventing the original master plan for Yarımca being followed (Petkim 1994).

PETKİM PRODUCTION, 1997

YARIMCA COMPLEX

PRODUCTS	CAPACITY	CAPACITY USE (%)	PRODUCTION (TONS)
Polyvinyl Chloride	55,000	99	54,317
L.D.Polyethylene	30,000	100	30,052
Polystyrene	27,000	107	28,947
Styrene butadiene rubber	33,000	86	28,265
Cis-polybutadiene rubber	20,000	95	18,911
Carbon Black	40,000	98	39,063
1,3-Butadiene	33,000	82	26,911
Rafinate			25,861
Vinyl Chloride Monomer	50,000	79	39,357
Ethylene dichloride			29,183
TOTAL	**288,000**	**92**	**320,867**

TABLE 1: production at Yarımca in 1997 Source : Petkim 1998

ALİAĞA COMPLEX

PRODUCTS	CAPACITY	CAPACITY USE (%)	PRODUCTION (TONS)
Ethylene	400,000	95	380,449
Polyvinyl Chloride	140,000	96	134,884
L.D.Polyethylene	180,000	107	192,852
H.D.Polyethylene	60,000	116	69,683
Polypropylene	80,000	105	83,617
Acrylonitrile	90,000	77	69,603
PTA	70,000	92	64,060
MEG	89,000	83	73,710
DEG			7,396
Caustic Soda (100%)			83,510
Propylene (KS)			80,680
Propylene (PS)			94,139
Vinyl Chloride Monomer	142,000	77	109,954
Chlorine	75,000	97	72,765
HCl (27%)			12,917
Phthalic anhydride	30,000	112	33,611
Benzene	123,000	94	115,087
o-Xylene			39,607
p-Xylene			106,518
Toluene			334
Hydrogenated Gasoline			91,852
C4 hydrocarbons			105,675
Gasoline			296,947
Liquid petrolem gas (LPG)			319
Aromatic Grease			62,643
MASTERBATCH	10,000	43	4,251
Ethylene dichloride			97,223
Plastic Products	8,000	86	6,862
TOTAL	**1,497,000**	**94**	**2,491,148**

TABLE 2: production at Aliağa in 1997 Source : Petkim 1998

2.2 Aliağa Complex

Aliağa Petrochemical Complex, which is 55 km north of Izmir, is the third biggest petrochemical complex of its kind in Europe. It has twelve main process factories and eight auxiliary units.

Aliağa was a fishing center until metal, petrochemical, paper and chemical fertiliser industries settled there in the 1980s. The area no longer has any attraction for vacationers even though the area includes the ancient city of Kyme and sandy beaches. The Foca region which is 25 km south of Aliağa is an important breeding area for the threatened Mediterranean Monk Seals.

The air pollution caused by the industries in the Aliağa area is visible by eye. The air emission control systems of the factories are totally inadequate. Some 9.7 ton/hour of SO_2 and 0.67 ton/hour NOx gases are emitted from the factories in the area (Muezzinoglu *et al.* 1994). Aliağa Petkim itself is responsible for almost half of these emissions.

Petkim Aliağa complex is a large PVC production site, manufacturing ethylene dichloride (EDC) and vinyl chloride monomer (VCM) as well as the final PVC product and chlorine and sodium hydroxide from the electrolytic separation of brine solution.

The Petkim plant, along with the shipyards and the petroleum refinery located nearby, pollute the sea with their discharges. Local fisherman report that the wastewater discharged by Petkim emits noticeable foul odours and sometimes causes massive deaths among fish. Petkim discharges more than 26,000 cubic meters of wastewater daily. Amazingly, although this industry produces and releases so much waste, it is self-regulating and not subject to any independent inspections (Muezzinoglu *et al.* 1994). Other wastes generated at the factories are sent to the treatment plant and the incinerator that operates at 800 degrees centigrade. Most of the hazardous wastes including the toxic ash of the incinerator are either stored on site or dumped on the environment.

Technologies currently available for the production of chlorine and caustic soda are based on mercury-cell, diaphragm or membrane processes. Petkim's Aliağa chlor-alkali unit is operated on mercury-cell process. The management agreed with the Trade Union of Petroleum Workers to change the system to the mercury-free membrane process. But none of the mercury-cells has been replaced to date.

3. GROWTH OF CHLORINE/PVC PRODUCTION IN TURKEY

Chlorine is produced at Seka in Dalaman, Ak-Kim in Yalova, Koruma Tarim in Izmit and Petkim in Aliağa. Petkim produced 72,765 tons of chlorine in 1997 (Petkim 1998). The process at Koruma Tarim is still based on mercury cells but replacement with membrane cells is being considered. Ak-Kim uses the membrane cell process. Both of these private companies have a capacity of 80 tons/day. Seka in Dalaman, which is a state-owned paper and pulp industry located in Dalaman produces chlorine with mercury cell process onsite for bleaching purposes. Chlorine dioxide is used for the bleaching and the wastewaters of the complex are discharged into the Mediterranean via a 6 kilometre long pipe. The factory has a capacity of 7,940 ton/year. The other complex of Seka in Izmit also has a chlorine plant but production is very limited and the closure of the factory is on the agenda due to environmental problems.

The chlorine produced at Petkim Aliağa complex is used for vinyl chloride

monomer (VCM) production on site. The capacity of the factory is 75,000 tons per year and only small amount of liquid chlorine is sold to the domestic market. Chlorine gas and sodium hydroxide (caustic soda) in liquid from is produced by electrolysis from salt produced from local sources. Chlorine is sent to the EDC/VCM plant under pressure. Caustic soda is stored in tanks at atmospheric pressure and sold on the Turkish market. VCM is the raw material for the production of polyvinyl chloride (PVC).

Petkim is the sole PVC producer in Turkey. Petkim produced 189,201 tons of PVC in 1997 (Petkim 1998). The licensors of the PVC factory are ICI, Solvay and Solvic.

In Turkey, PVC is widely used in the construction field (pipes, for example). It is also used in packaging, profiles, toys, hospital supplies, floor coverings, cables, bottles, and many other products. In 1985 the production of PVC was 42,019 tons (DPT 1990). In only 12 years this amount increased almost five-fold and reached almost 190,000 tons. Between 1985 and 1995 the annual average increase in PVC production was therefore 9.9% (Petkim 1997). After the liberalisation of the Turkish economy in the first half of 1980s plastic consumption rapidly increased. In 1985 the consumption of low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), polypropylene (PP) and PVC plastics per capita was 5.82 kg (DPT1990). According to 1996 figures this amount has increased to 21 kg per capita. The demand increase rate in the last 10 years was 12% per year according to information from the state statistics institute (DIE).

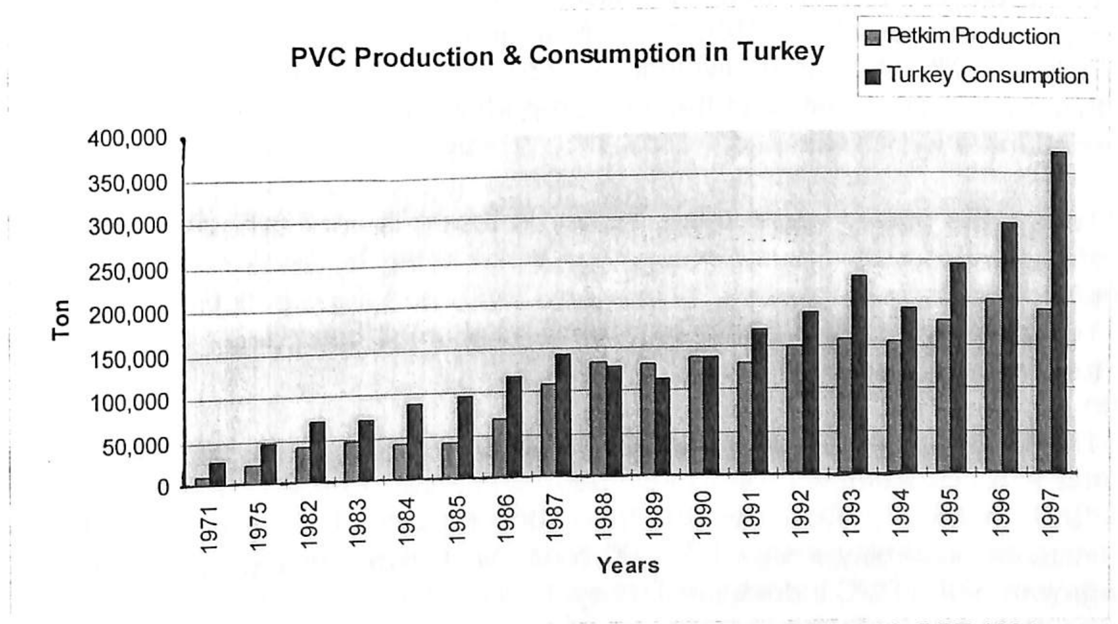


FIGURE 2: PVC production and consumption in Turkey Sources: DPT 1990; DPT 1994; DIE(1998)

Since 1985 the consumption of polyethylene and PVC increased significantly. Today, PVC is one of the most widely used plastics. The hazards of this plastic are not well known among the public. Developments in the construction field in Turkey and in international trade increased income for the

PVC market. While it was mentioned in the 6th Development Plan that the PVC profiles were more expensive than wooden and aluminium profiles (DTP 1990), today the prices are lower than the others and the PVC profile market is increasing rapidly.

Before the liberalisation of the Turkish economy, most beverage containers where refillable glass bottles, but subsequently the industry shifted to disposable plastic bottles. In response to opposition from the environmental groups the government formulated a quota system for disposable plastic containers under which all companies selling their products in disposal plastic, metal or glass containers should collect a specified amount of used containers for recycling. In the plastics sector, the main competitor to PVC bottles is PET bottles but, particularly in the vegetable oil and other food, beverage and detergent sectors, PVC is still widely used. Table 3 indicates the projection for disposable plastic containers to be collected back and recycled.

Year	Plastic
1992	25%
1993	35%
1994	45%
1995	65%
1996	70%

TABLE 3: Targets for recycling of disposable plastic containers. Source: DPT (1994).

The projected figures were unrealistic in practical terms and have not been met. Consequently, in 1997 the official quota for plastics was dropped from 70% to 30% which is equivalent to 13300 tons/year. It is unlikely that even this quota will be met and the vast proportion of disposable plastic and PVC containers will be dumped.

Today, the plastic waste crisis Turkey is facing is very serious since the 3R strategy (Reduce, Reuse, Recycling) is not being implemented. Processing of post-consumer plastics, particularly PVC, is a very polluting business in Turkey today as it is being carried by very small companies operating with totally inadequate technology.

The PVC market in Turkey is growing rapidly in other fields as well. Although the PVC consumption of Turkey was estimated to be 231.660 tons/year for 1997 in the 7th Development Plan, according to DIE, the state statistics institute, in reality it was 374,000 tons. This also indicates the unexpected growth of the PVC industry in Turkey.

As a result of these developments the market share of Petkim started to fall. While the market share of Petkim for PVC in 1989 was 83%, this percentage dropped to 66% in 1996 (Petkim 1997). Consequently a third petrochemical complex project is on the agenda today. The feasibility study for the third complex proposes a capacity for the new chlor-alkali factory of 500,000 ton/year, with 161,000 ton/year of VCM and 160,000 ton/year of PVC capacity (Petkim 1997).

Since 1987, like many other state-owned giants, Petkim has been on the agenda of the government for privatisation. The government wants to transfer the control of the management to a petrochemical company or another bidder through a block sale. But there are also other proposals for the privatisation of Petkim. The following corporations have expressed interest; Amoco (USA), Degussa (Germany), Elf (France), Dow Chemical (USA), Goodyear (USA), Union Carbide (USA), Marubeni (Japan), Enichem (Italy), Phillips (India), Sabanci (Turkey), Dinckok (Turkey) (Egilmez 1997). However, the Petroleum Affairs Union, with many other Unions and Chambers, is campaigning against the privatisation of Petkim.

4. PROCESS AND PROBLEMS

4.1 The chlor-alkali process

This process is used to manufacture sodium hydroxide and chlorine gas. Sodium hydroxide is a widely used bulk chemical. Chlorine and its uses are described in more detail below.

The basic chemical reaction is to convert common salt and water into sodium hydroxide, chlorine gas and hydrogen gas. This is done by passing electricity though a salt water solution (brine). The overall chemical equation is:

$$2NaCl + 2\,H_2O \qquad 2NaOH + Cl_2 + H_2$$

4.1.1 Mercury

There are three main chloralkali processes. At its Aliağa plant, Petkim currently uses the most polluting technology- the mercury cell.

Mercury will inevitably be released from this process. It will contaminate the local environment (Rule & Iwashchenko 1994, Bertani *et al.* 1994), food chain (Bertani *et al.* 1994) and the workers (Barregard *et al.* 1994).

Mercury is a highly toxic, bioaccumulative and persistent metal. It has no beneficial effects in humans. Any long term exposure may therefore be expected to progressively cause severe disruptions in the normal functions of any accumulating organ (Nriagu 1988) including the kidneys, liver and the central nervous system. Inhalation of mercury vapour may produce an acute, corrosive bronchitis and interstitial pneumonitis and, if not fatal, may be associated with symptoms of central nervous system effects such as tremor or increasing excitability. The bulk of information available does suggest that the most sensitive target of inhalation exposure to metallic mercury is the central nervous system (ATSDR 1993a).

Long term exposure to either inorganic or organic mercury can also result in permanent damage to the kidneys. The kidney appears to be the most sensitive organ following oral exposure. In addition to the sensitive systems mentioned above, mercury may adversely affect a wide range of other organs systems if exposure is sufficiently high. Affected systems include the immune, respiratory, cardiovascular, gastrointestinal, hematological and reproductive systems (ATSDR 1993a).

In the US, it was estimated that the chlor-alkali process resulted in the release of 5.9 Mg of mercury to the atmosphere in 1990 (Pai *et al.* 1998). The international body which controls the pollution of the North-east Atlantic has recommended:

....that existing mercury cell chlor-alkali plants be phased out as soon as practicable. The objective is that they should be phased out completely by 2010 (PARCOM 1990).

Because of the concern about mercury, Greenpeace has conducted surveys of mercury in and around the Aliağa Petkim plant. Environmental samples demonstrate contamination with mercury and effluent samples confirm that Petkim is the source.

Sample number and date	Location of sample	Mercury concentration
Aqueous samples		**ug/l**
MI6152/24-9-96	outfall 1	<2
MI6153/24-9-96	adjacent to outfall 2	255
Solid samples		**mg/kg dry wt**
MI6147/ 23-9-96	banks of effluent canal, outfall 1	1137.0
MI6148/23-9-96	10-15m from outfall 1	513.9
MI6149/23-9-96	10-15m from outfall 1	459.2
MI6150/23-9-96	20-25m from outfall 2	403.4
MI6151/23-9-96	20-25m from outfall 2	409.8
MI8007/01-5-97	coastal dump site	0.3
MI8009/01-5-98	coastal dump site	7.1
MI8010/01-5-98	coastal dump site	1.4
MI8015/01-5-98	coastal dump site	2.9

TABLE 4: Concentration of mercury contamination in and around Petkim

EC Directive 85/613/EEC states that when mercury is used in the chlor-alkali industry, effluents discharged must not contain more than 50 ug/l (parts per billion) of mercury. Although this standard does not apply to Turkey, the fact that such a low permissible limit is set for Europe should indicate how potentially harmful this metal is. Sea water sampled adjacent to outfall 2 contained 255 ug/l of mercury- over five times the EU limit. Sediments collected near the outfalls contain up to 2,000 times published background concentrations (Bryan & Langston 1992).

Mercury in sediments will be converted to methylmercury by bacteria. It can biomagnify through the food chain, so aquatic invertebrates, fish and birds

feeding from polluted sites may all be exposed. Fish (including shellfish) can accumulate high levels of mercury compared with other aquatic species (ATSDR 1989). The bioconcentration factor of methylmercury in fish to that in water is usually between 10,000 and 100,000 (WHO, 1990), and it is through eating fish (including shellfish and fish products) that most people are likely to accumulate methylmercury from the environment.

However, for chlor-alkali process workers, there is likely to be another accumulation route. They could be exposed to inorganic compounds of mercury (including elemental mercury vapour) within the factory. To investigate mercury exposure of workers at Aliağa, Greenpeace conducted analyses of human hair in 1997 (Stephenson 1997). Hair is regarded as a good biomarker of long term exposure to mercury, including occupational exposures (ATSDR 1993a, WHO 1990).

Samples were taken from 54 men who worked at different sites in the factory. Results are presented in figure 4 below. Study subjects are classified according to the area of the factory where they worked, either at the time of the study or at some earlier point in time. Zone 1 refers to the immediate area of the mercury cells; workers in this area will include the mercury cell operators and mechanics. Zone two includes the areas adjacent to the cells, where workers make up brine. There will be some mercury contamination of this area as mercury is carried out of the cells in products and effluents. Zone three is all zones away from the mercury cells. It is worth noting that some workers- particularly maintenance staff- operate in more than one zone. In their case, and in the case of workers who have had more than one job within the plant over the course of their careers, all zones worked in are listed.

Mercury levels in the hair of the chlor-alkali workers sampled range from 0.2 to 18.6 mg/kg, with a mean value of 2.25 mg/kg. Control samples taken from individuals both in Turkey and the UK were at the extreme low end of the results for this study. Among the Petkim workers, the lowest levels were generally seen in those persons infrequently exposed to mercury, particularly those who only worked in zone 3. At the other end of the scale, all workers whose hair contained more than 1.8 mg/kg mercury had worked in zone 1 at least some of the time.

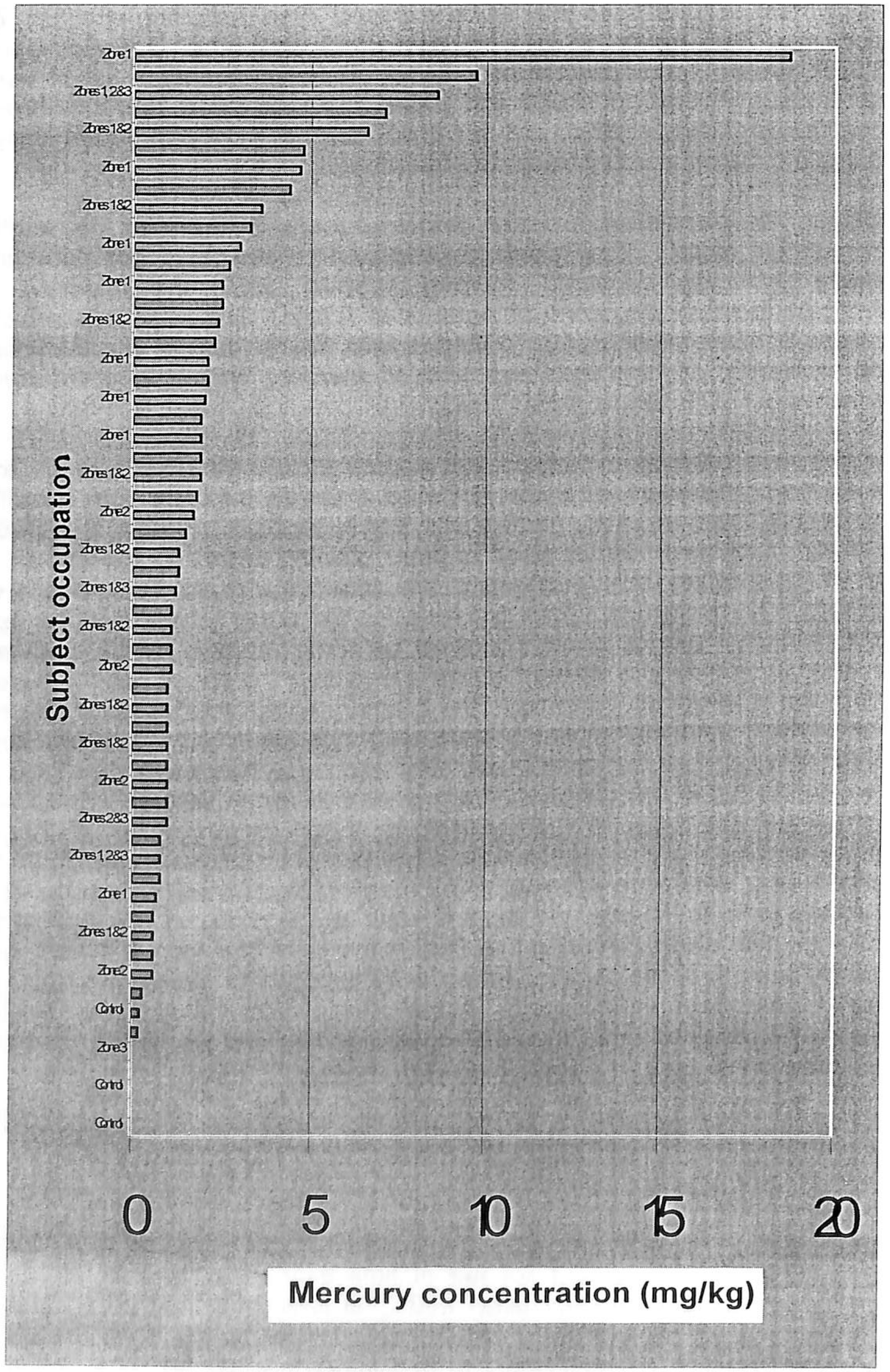


FIGURE 3: The concentrations of mercury found in individuals working at different sites at the Aliağa plant.

There is little published data on hair levels of mercury in chlor-alkali workers, but data published on mercury levels found in gold miners and in persons consuming methylmercury contaminated fish (Abe 1995, Barbosa 1995, Palheta, 1995). For example, a population exposed to methylmercury contaminated fish (Haxton 1979), had mercury hair levels surrounding a mean value of 2.0 mg/kg. A maximum level of 11.3 mg/kg was detected. A study on mercury levels in the hair of Brazilian gold miners showed levels ranging from 0.4 to 32.0 mg/kg, with no mercury being detected in the control population studied (Palheta 1995). Thus, the hair mercury concentrations of the Petkim workers is in line with that of other highly exposed workers. As mentioned above, there have been proposals to switch to membrane technology in this process, but until the mercury cells have been closed down, the health of all the workers exposed will continue to be at risk.

4.1.2 Chlorine and organochlorines

Chlorine was first synthesised in the laboratory in 1774, but H. Davy was to first to recognise it as a chemical element in 1808 and named it from the Greek chloros, meaning greenish yellow (Gerhartz 1986). Under normal conditions, it is a gas and is notorious for having been used as a chemical weapon in the First World War. It is intensely irritating and causes oedema of the lungs (production of fluid in the lungs), and exposure can be rapidly fatal. The first chlorine gas attack took place against the Russians on January 19th 1915, but the attack does not appear to have been very successful and no warning was passed to their allies (Marshall 1987). The second attack, on 22nd April 1915, at Ypres in Belgium, was more successful though there are varying estimates of the numbers killed. Some estimate that 5000 soldiers were killed, but others believe the figure was nearer 1000 (Marshall 1987, Marrs *et al.* 1996). The British forces retaliated with their first chlorine gas attack in September 1915 (Marrs *et al.* 1996).

Since the First World War, there have been numerous releases of chlorine from industrial facilities, many of them resulting in deaths (Marshall 1987).

Apart from PVC, chlorine is also used to manufacture thousands of organochlorine products. Organochlorines are materials based on carbon and chlorine. Initially regarded as a technological advancement, many have been restricted or banned because of their potential harm to human health and the environment. The most notorious of the orgnochlorines include the insecticide DDT, the ozone depleting CFCs, chlorinated solvents including dry cleaning fluids, PCB transformer fluids, and dioxins and furans which are the world's most toxic organic pollutants. PVC and its precursors ethylene dichloride and vinyl chloride are all organochlorines.

4.2 Ethylene dichloride and vinyl chloride

The next stage of PVC manufacture is to make ethylene dichloride (EDC). This is then converted into vinyl chloride, which is the basic building block (monomer) for PVC. EDC can be produced by oxychlorination or by direct chlorination. In the direct chlorination method, ethylene is reacted with chlorine to produce EDC. Oxychlorination produces EDC by reacting ethylene with dry hydrogen chloride and oxygen (ATSDR 1995a).

To produce vinyl chloride (VC), EDC is subjected to high pressures and temperatures. This causes the EDC to undergo pyrolysis (also called thermal cracking), which yields vinyl chloride monomer and hydrogen chloride.

Both ethylene dichloride and vinyl chloride monomer are hazardous chemicals. Their production also results in the generation of toxic chlorinated wastes containing dozens of hazardous chemicals. This waste also contains dioxins, some of the most toxic chemicals produced by modern industry.

4.2.1. Ethylene dichloride

Ethylene dichloride is a colourless, volatile liquid with a pleasant smell. Its proper chemical name is 1,2-dichloroethane but it is more commonly called ethylene dichloride or EDC. It will not persist very long in the environment, but is both hazardous and toxic. It is highly flammable and may pose an explosion hazard.

Because of its volatility, the most usual route of exposure is via inhalation. However, it can also cause harm through skin contact or eye contact. It is one of the more toxic chlorinated solvents via inhalation. At high concentrations, it can upset the nervous system and gastrointestinal system, causing dizziness, nausea and vomiting. The liver, kidney and adrenal gland may also be damaged. EDC can be toxic at concentrations too low to be detected by smell (Snedecor 1993).

4.2.2 Vinyl chloride

Vinyl chloride is a colourless, sweet smelling gas under normal conditions. In the US in 1992, 98% of vinyl chloride was used to make PVC. As with EDC, it does not persist long in the environment, but it is still hazardous. Mixed with air, it can be explosive and it causes a wide variety of toxic effects in humans and animals. It is a known human carcinogen (Group 1 as assessed by the International Agency for Research on Cancer, IARC). Numerous studies demonstrate that it causes angiosarcoma of the liver in the occupationally exposed and other studies have shown elevated levels of cancers of the brain and nervous system, lung and respiratory tract and the lymphatic/haemapoietic system although the evidence is less strong. There are less well supported indications of cancers at still further sites (ATSDR 1995a).

Not surprisingly, the most usual route of exposure for vinyl chloride is via inhalation. Studies of workers who breathe in vinyl chloride are complicated because they often also smoke and would also tend to be exposed to PVC dust which can harm the lungs. However, it appears to cause emphysema, dyspnea, pulmonary lesions and a number of other health problems with the lungs. As noted above, there is some evidence of lung cancer (ATSDR

1995a).

Exposure to high levels of vinyl chloride can cause Raynaud's phenomenon, where the blood circulation in worker's fingers is damaged so that they become white and painful in cold conditions. This illness is sometimes followed by resorption of the bones in the tips of the fingers or lesions on bones in other parts of the body (ATSDR 1995a).

Workers have also been reported to die more frequently from cardiovascular and cerebrovascular disease (eg heart attacks and strokes). Vinyl chloride can also reduce blood's ability to clot normally (ATSDR 1995a).

Vinyl chloride is narcotic and inhalation can cause dizziness, headaches, drowsiness or unconsciousness, euphoria, memory loss, visual and/or hearing disturbances, sleep disturbance, nausea, irritability and nervousness. Damage to the nervous system manifests itself in peripheral neuropathy with tingling, pain or numbness in the fingers (ATSDR 1995a).

Toxic effects are also seen on the immune systems, livers, spleens, thyroid function, eyes and skin of workers. Anorexia (weight loss) has also been reported and there are some indications that vinyl chloride can affect the reproductive systems of both men and women (ATSDR 1995a).

4.2.3 EDC/VCM wastes

Wastes from the production of EDC/vinyl chloride are complex and variable in nature. "Light ends" from the purification of EDC are volatile liquids whereas "heavy ends" or EDC tars are thick black liquids. Many of these wastes will be contaminated with dioxins. ICI, for many years the UK's major EDC and vinyl chloride manufacturers, stated that the oxychlorination process inevitably produced dioxins (ICI 1994). Many other pollutants may also be present in the wastes; these are also considered below.

4.2.3.1 Dioxins and furans

The terms "dioxin" or "dioxins and furans" generally refers to a group of 210 chlorinated pollutants, the polychlorinated dibenzo-p-dioxins and dibenzofurans. They are widely regarded as the most toxic organochlorine pollutants. They are also highly persistent in the environment. They have always been produced naturally in very small quantities. However, in modern times, they have also been produced as byproducts of industrial processes involving chlorine. Today, industrial sources far outweigh natural ones, with the result that background concentrations of dioxins and furans are far higher than a hundred years or more ago (see eg Alcock *et al.* 1998).

In addition to being highly persistent in the environment, dioxins and furans are fat soluble. Consequently, they build up in the bodies of animals and remain there for many years. Every person alive is exposed to dioxins on a daily basis.

The most toxic of the 210, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), is used as the toxicological model for the group and has been very extensively researched. There are 17 dioxins and furans that have the 2,3,7,8-chlorine substitution and consequently act through the same biochemical mechanism. Their toxicity is rated against that of 2,3,7,8-TCDD and each compound is given a toxicity equivalence factor (TEF). This system allows the scientist to estimate the total toxicity of the mixes of dioxins and furans as a 2,3,7,8,-TCDD toxicity equivalent (TEQ). Analytical results for dioxins are therefore usually expressed in terms of the TEQ.

2,3,7,8-TCDD has been classified in group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC)(IARC 1997).

The most extensive review of the toxicity of 2,3,7,8-TCDD was conducted by the US Environmental Protection Agency (USEPA) and published in draft form in 1994 (USEPA 1994a). It found that in addition to causing cancer, dioxin could damage the nervous system, the immune system, the reproductive system (including reducing sperm count), cause malformations in the unborn, disrupt the endocrine system and cause a number of other effects.

Most importantly, the draft review concluded that some of the more sensitive effects could be occurring at the levels of exposure that are experienced by ordinary men and women. It suggested that a daily intake of 0.01pg TEQ/kg body weight per day for humans would results in one extra cancer in a million people over the course of a lifetime. This is considerably lower (300-600 times lower) that the ordinary exposure, which the USEPA estimated at that time at 3-6 pg TEQ/kg body weight per day. It was therefore thought plausible that dioxin exposure could be causing cancer in 1 in 1000 to 1 in 10000 people (USEPA 1994a).

More recently, the WHO re-evaluated the tolerable daily intake (TDI) of dioxins and furans for the ordinary population. They recommended that the TDI be reduced from 10pg/kg body weight/day to 1 to 4 pg/kg body weight. They also recognised that background exposure in developed countries is higher than this TDI, being 2-6 pg/kg body weight/day and recommended that every effort should be made to reduce exposure to the lowest level (WHO 1998).

Since dioxins are very poorly soluble in water, they will only be present in aqueous effluents in very low concentrations. However some of the wastes from the PVC industry can contain high concentrations of dioxins.

In 1997, Greenpeace analysed a sample of Petkim Aliağa waste for dioxins. The results are given in the table below.

	Toxicity Factors ITEF	**Reported results (ug/kg dry wt)**	**Toxicity Equivalents (ITEQ) (ug/kg dry wt)**
Dioxins			
2378-TCDD	1	0	0
12378-PeCDD	0.5	0.34	0.17
123478-HxCDD	0.1	0.39	0.039
123678-HxCDD	0.1	0.34	0.034
123789-HxCDD	0.1	0.33	0.033
1234678-HpCDD	0.01	4.9	0.049
OCDD	0.001	25	0.025
Furans			
2378-TCDF	0.1	1.4	0.14
12378-PeCDF	0.05	22	1.1
23478-PeCDF	0.5	4.9	2.45
123478-HxCDF	0.1	190	19
123678-HxCDF	0.1	51	5.1
123789-HxCDF	0.1	48	4.8
234678-HxCDF	0.1	12	1.2
1234678-HpCDF	0.01	1200	12
1234789-HpCDF	0.01	240	2.4
OCDF	0.001	8400	8.4
		Total ITEQ	**56.94 ug/kg dry wt**

TABLE 5: Results of dioxin analysis of waste from Petkim.

The sample from Petkim must be regarded as extraordinarily highly contaminated. As an example, the USEPA (USEPA 1994b) summarised all the available data for soils in the US and Europe. They found that in the US, a background soil sample, with no particular industrial contamination, contained on average, 8 ng/kg TEQ PCDD/F. In Europe, the average figure was 9ng/kg TEQ.

This means that the sample taken at Petkim contained between 6 and 7 thousand times more than uncontaminated soil- clearly a very hazardous waste indeed.

The dioxin contamination seen in Aliağa is typical of that from PVC factories- it contains the same "fingerprint" of different dioxin and furan congeners seen at other PVC factories (see *eg.* ICI 1994, Wenning 1992), with a very high proportion of higher chlorinated dibenzofurans. Greenpeace and other researchers have analysed samples associated with VCM or PVC manufacture. The data are given in the table below. They demonstrate that the waste collected from Petkim is among the most contaminated samples recorded from this industry.

Sample type	VCM/PVC producer	Country	ITEQ (ng/kg)	Sample number and reference
mussel	Enichem	Italy	6.89	MI 5123/ Greenpeace data
sediment	Geon Goodrich	USA	15.42	PU4033/ Greenpeace data
organic waste	Borden	USA	329	MI6049/ Greenpeace data
sediment	Akzo	Netherlands	433	J2/ Wenning *et al.* 1992
sediment	Akzo	Netherlands	683	J5/ Wenning *et al.* 1992
sediment	Akzo	Netherlands	715	J1/ Wenning *et al.* 1992
sediment	Enichem	Italy	753.5	MI5021/ Greenpeace data
sediment	Akzo	Netherlands	835	J4/Wenning *et al.* 1992
sediment	Akzo	Netherlands	922	J3/ Wenning *et al.* 1992
organic waste	Formosa Chemicals	USA	3192	PU4043/ Stringer *et al.* 1995/ Greenpeace data
organic waste	ICI	UK	7561	MOPS VH/2A ICI 1994
sediment	ICI	UK	12286	MOPS/L1/1A ICI 1994
organic waste	EVC	UK	16530	UK6003/ Greenpeace data
organic waste	Georgia Gulf	USA	19978	PU4016/ Stringer *et al.* 1995/ Greenpeace data
sediment	Aiscondel	Spain	48000	MI5059/ Greenpeace data
sludge	**Petkim**	**Turkey**	**56940**	**MI4047/ Greenpeace data**
sludge	PPG	USA	76239	MI6051/ Greenpeace data
organic waste	Vulcan Chemical	USA	6370000	PU4017/ Stringer *et al.* 1995/ Greenpeace data

TABLE 6: Dioxin contamination of Petkim wastes compared to other PVC-related wastes from around the world.

4.2.3.2 Other chlorinated and non-chlorinated pollutants

Although dioxins are the most notorious and best researched pollutants found in PVC industry wastes, there are literally hundreds of other pollutants mixed in with them. These may be released to the environment in a number of ways, including in the wastewater emitted from the plant.

Since 1996, Greenpeace has analysed samples of wastes, wastewater and sediments from the Aliağa sites and its immediate environment. This includes samples from the on-site incinerator, sediment from the bay and samples taken from an apparently uncontrolled dumpsite in the plant area near the coast. The table below lists the chlorinated pollutants found in these samples and identified with a certainty of more than 90% by computer-based mass spectral matching techniques.

1,1,2,3,3-Pentachloro-1-propene	Benzene, chloro(2-chloroethyl)-
1,1'-Biphenyl, 2,2',3,3',4,4',5,5',6-nonachloro-	Benzene, hexachloro-
1,1'-Biphenyl, 4-chloro-	Benzene, pentachloro-
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	Benzene, pentachloro(trichloroethenyl)-
1,3-Butadiene, 1,1,3,4-tetrachloro-	Benzenemethanol, 4-chloro-3-nitro-
1,3-Butadiene, pentachloro-	Butane, 1,2,3,4-tetrachloro-
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-	Chloroform
1-Butene, 1,4-dichloro-	Chloromethyldiphenylmethane
1-Butyne, 3-chloro-	Ethane, 1,1,2,2-tetrachloro-
1-Propene, 3,3,3-trichloro-2-methyl-	Ethane, 1,1,2-trichloro-
1-Propene, pentachloro-	Ethane, 1,2-dichloro-
2,2-Chlorophenyl-1,1-dichloroethylene	Ethane, hexachloro-
2-Butene, 1,4-dichloro-	Ethane, pentachloro-
Benzene, (2-chloroethenyl)-	Ethene, tetrachloro-
Benzene, (2-chloroethyl)-	N-(3'-Chlorophenyl)-2-hydroxyimino acetamide
Benzene, 1,2,4-trichloro-	o,p'-DDT
Benzene, 1,2-dichloro-	Octachloropentafulvalence
Benzene, 1,4-dichloro-	Octadecane, 1-chloro-
Benzene, 1-chloro-2-(1-chloroethyl)-	Phenol, 4-amino-2,6-dichloro-
Benzene, 1-chloro-2-ethyl-	Phenol, 4-chloro-5-methyl-2-nitro-
Benzene, 1-chloro-2-methyl-	Propane, 2-bromo-1-chloro-
Benzene, 1-chloro-3-ethyl-	Propane, 3-chloro-1,1,1-trifluoro-
Benzene, 1-chloro-4-ethyl-	Sulfone, chloro phenyl
Benzene, chloro-	

TABLE 7 Organochlorine pollutants identified in environmental and waste samples taken from the site and vicinity of the Aliağa Petkim site since 1996.

It is not possible to find research on the toxicity of all the chemicals present in these samples- though many are well known for their toxicity. The Petkim samples contain a number of chemicals listed for control under the North Sea Ministerial declaration (MINDEC 1990) and the Barcelona Convention strategic action programme to address pollution from land-based activities (UNEP 1995).

Interestingly, two isomers of the PCBs are also identified (2,2',3,3',4,4',5,5',6-nonachloro-1,1'-biphenyl and, 4-chloro-1,1'-biphenyl). The environmental problems of the PCBs are undisputed and has lead to their being phased out of production almost all over the world. It is impossible to tell what the source of these congeners is, but it is possible that they, like the dioxins, are byproducts of the chemical reactions taking place during synthesis and purification of EDC and VCM.

4.3. PVC and its additives

PVC dust can damage the lungs of workers (Lee *et al.* 1989, Studnicka *et al.* 1995) and "meat-wrappers asthma" has been known since the 1970s to result from working with PVC packaging.

More recently, a preliminary Swedish study showed that workers who reported having worked with PVC had a greater chance of contracting testicular cancer (Hardell *et al.* 1997). More research is needed to confirm these findings but they raise serious concerns nevertheless.

PVC on its own is brittle and of little use for making products; it is therefore always mixed with additives (Ehrig 1992). Matthews (1996) describes many of the additives used in PVC; there are too many to list here. The most toxic ones include:

lead compounds (stabilisers);
cadmium compounds (stabilisers);
other metal compounds (stabilisers);
organotin compounds (stabilisers);
phthalates (plasticisers);
chlorinated paraffins (plasticiser extenders);
antimony compounds (flame retardants)

4.3.1 Lead compounds

Lead compounds used as stabilisers can be released from the product, a fact that has caused concern because of the toxicity of lead, especially to children. In Canada in 1996, numerous newspaper reports told the story of window blinds being removed from sale after the discovery that sunlight would cause the PVC to degrade and release lead. It was thought that the lead dust could be particularly hazardous to children under the age of six.

Lead may also be released from the plastic during its recycling or disposal, though this subject has not been extensively researched. Members of the PVC industry, however, are aware of the problems with lead; PVC coated cables seem especially worrying to the industry (Carroll *et al.* 1992).

4.3.2. Cadmium compounds

Cadmium is a highly toxic metal that is used to stabilise PVC in some applications and also as a pigment in PVC and other applications (Tamaddon & Hogland 1993). Window frames are frequently stabilised with cadmium compounds (Matthews 1996). Cadmium use in plastics has been banned in Sweden (Tamaddon & Hogland 1993) and restricted in Switzerland and the EU for environmental reasons (Vollrath *et al.* 1992). PVC is the only plastic in which cadmium is used as a stabiliser (Tamaddon & Hogland 1993).

4.3.3 Chlorinated paraffins

Chlorinated paraffins are frequently used in PVC coating for electrical cables; when present they tend to represent 10% by weight of the PVC formulation (Matthews 1996). Chlorinated paraffins are ecotoxic compounds which have long been recognised as highly persistent in the environment, bioaccumulative and transported globally from the point of release (see e.g. Svanberg 1983). The Oslo and Paris Commissions agreed in 1996 to phase out long chain chlorinated paraffins in the North East Atlantic countries.

4.3.4 Antimony compounds

Antimony trioxide is present as a flame retardant. It is toxic and suspected of being carcinogenic (Matthews 1996).

4.3.5 Phthalate plasticisers

The phthalate esters are a family of compounds which are the most widely used PVC softeners (Bizzari *et al.* 1996). They are persistent in the environment and are the most abundant man-made chemicals in the environment (Jobling *et al.* 1995). They can bioaccumulate to some degree, predominantly from food. They also exhibit a variety of toxic effects, based on research in animals.

Some phthalates can cause cancer in animals and the most common one, DEHP, has been classified as possibly carcinogenic to humans by the IARC (IARC 1987, ATSDR 1993b, European Commission 1996). Some can also affect the liver (Chan & Meek 1994, ATSDR 1990& 1995b, Swedish National Chemicals Inspectorate (KEMI) 1994); the kidneys (Chan & Meek 1994, ATSDR 1990 & 1993b) and irritate the eyes (ATSDR 1995b).

Individual phthalates can harm the male reproductive tract (Chan & Meek 1994, ATSDR 1995b & 1993b); the female reproductive tract (Chan & Meek 1994, Ema *et al.* 1994, ATSDR 1993b); impair reproductive success (Chan & Meek 1994, Ema *et al.* 1994 & 1995, ATSDR 1990, 1993b & 1995b) and cause teratogenicity (malformation of the offspring)(Ema *et al.* 1993 & 1995, Chan & Meek 1994, ATSDR 1993b & 1995b).

Because of concern about the toxicity of the phthalate plasticisers and their use in products used for children, Greenpeace analysed teethers and other toys from a number of countries. They contained high levels of phthalates; as much as 40% in some items (Stringer *et al.* 1997), in addition to a wide range of other additives and contaminants, many of which simply could not be identified. Other researchers found that unacceptable concentrations of some of the phthalates could leach from some of the toys, and certain PVC toys have been removed from sale in a number of European countries (see eg MacKenzie 1997). The European Commission has been discussing potential restrictions in the use of phthalates in children's toys (see eg CSTEE 1998); but at the time of writing no conclusion had been reached.

Another suspected source of harm to people- particularly children- is from breathing in phthalates. Recent research has suggested that atmospheric DEHP could have a role in asthma in children (Oie *et al.* 1997).

4.4 Recycling of PVC

Greenpeace has investigated the PVC recycling issue in depth. Only a tiny fraction of PVC is actually recycled, since there are numerous technical problems and the process is not economically viable (van der Naald & Thorpe 1998). In Europe, PVC has the lowest recycling rate and post-consumer recycling amounts to only 0.6% of the total PVC consumption in Europe

(SOFRES 1995). In Australia the post-consumer PVC recycling is only approximately 0.25% of PVC consumption and lower than other commodity plastics (BIE 1994).

Toxic additives in PVC can either be released to the environment during recycling or contaminate recycled products. For example, lead is not usually used in PVC flooring, but was present in recycled PVC flooring bought in Germany and analysed by Greenpeace.

Moreover, the presence of PVC in a plastic waste stream can severely damage the recycling of other plastics. For example, PVC is hard to separate from PET by the commonly used method of flotation. PVC that remains in a PET waste stream will char at the PET processing temperatures and spoil the recycled PET (Ehrig, 1992). The Association of Postconsumer Plastics Recyclers (APR) in the USA considers PVC a contaminant to PET and HDPE reprocessing. According to the APR, 'PVC bottles have no place in post-consumer plastic bottle recycling' (APR 1998).

4.5 Disposal of PVC

The toxic additives in PVC can continue to cause problems even during disposal processes.

Municipal incinerators are a major source of atmospheric dioxins and furans (see eg USEPA 1994b). The chlorine in the PVC may contribute to the formation of dioxins though the amount created and emitted will vary from incinerator to incinerator. Much of the chlorine present will be converted to hydrogen chloride, an acidic gas, in the incineration process. To prevent it being released to the environment, modern incinerators neutralise it with lime (calcium carbonate) or caustic soda (sodium hydroxide) creating salts. Incineration of 1kg of PVC with dry or semi-dry scrubbers results in 1.7-3.0 kg of residual salts that need to be disposed of as hazardous waste (Rasmussen 1995, Moller *et al.* 1996). According to the Danish PVC industry it generates even more: 2-5 kg residual waste per kg PVC. One other study gives a figure of approximately 0.9 kg residual salts. Wet scrubbers form highly saline waste water and sludge (Moller *et al.* 1996) which, of course, must also be disposed of. Thus, incineration of PVC can increase the waste problem rather than decrease it.

PVC contributes 30-40% of the cadmium in municipal solid waste (MSW). It is easily volatilised during the incineration process and forms cadmium chloride; 90% of which is trapped in filter dusts. However, there is a significant risk of cadmium leaching from these dusts, especially in an acid environment (Tamaddon & Hogland 1993). Lead and other metals used in PVC will also be released to the environment and sequestered in incineration ash in the same way.

Electrical cables coated in PVC are often smelted to recover the copper. This can cause significant dioxin contamination as the PVC burns (Harnly *et al.* 1995, Huang *et al.* 1992, Liem *et al.* 1990, Lu *et al.* 1995a&b).

As noted earlier, lead creates problems with the disposal of cables. Indeed, it leaches to such an extent that cables often cannot be landfilled in the US (Reith 1996, Carroll *et al.* 1992). Phthalates will also leach from landfilled PVC to a significant extent (Wams 1987).

PVC presents a particular hazard during accidental fires because of the inevitable release of a number of highly toxic substances. A fire in a West Delhi plastic scrap market affected a quarter of the city and resulted in a greatly enhanced deposition of a number of polluting species. In particular, the deposition of 21 tonnes of chlorine was attributed to the pyrolysis of PVC (Jain *et al.* 1996). The Municipal Corporation of Delhi has been directed by the High Court in Delhi to enforce a ban on waste PVC trading and stockpiling at and nearby the market (Asian Chemical News 1996). Hydrochloric acid (HCl) emitted during the burning of PVC can be a major hazard to fire fighters (Meharg 1994). Other toxic chemicals released on combustion of PVC include dioxins, furans, PCBs, chlorotoluene, chlorophenol, and aromatic and polynuclear aromatic organic compounds; lead, cadmium, antimony and zinc compounds (Meharg 1994, Meharg & French 1995).

5. THE BARCELONA CONVENTION PROTOCOL FOR THE PROTECTION OF THE MEDITERRANEAN SEA AGAINST POLLUTION FROM LAND-BASED SOURCES

This Protocol was adopted in 1980, entered into force in 1983 and was last amended in 1995 in an effort to prevent the pollution of the Mediterranean Sea from the hazardous discharges coming from the surrounding countries either directly through land and air or through other indirect streams.

The Barcelona Convention LBS Protocol needs local, national and international action to deal with the problems of hazardous waste streams in a comprehensive way. Countries must adopt the precautionary princible, which means that pollution must be stopped even if there is not full scientific proof that it is damaging human health or the environment. This is an important step on the way to achieving the cherished goal of sustainable development.

International obligations are contracted at the national level and should be followed and implemented at all administrative levels. In order to facilitate this process, a strategic action programme (UNEP 1995) has been agreed which outlines priority pollutants and identifies pollution "hot spots" where urgent action is required.

Turkey is a Party to this protocol and has signed its latest amendments but has not ratified yet. In order for the Convention to enter into force, three quarters of the Mediterranean Countries must ratify all the protocols and the amendments of the Barcelona Convention. In virtue of the protocol and in accordance with the 1995 Barcelona Resolution, substances which are toxic, persistent and liable to bioaccumulate in the environment, particularly organohalogens, should be reduced to the minimum by the year 2005.

Similarly, each country has to prepare an action plan containing measures and timetables to eliminate pollution to the marine environment from these substances as listed in annex I of the Protocol. Both mercury (a heavy metal) and organohalogens (which include the organochlorines identified at Petkim) are in Annex I.

6. CONCLUSIONS

Production of chlorine and PVC at Aliağa have resulted in contamination of members of the workforce and environment. A similar picture may be expected at Yarımca where similar processes have been used in the past. The life cycle of PVC inevitably involves hazardous materials, including a number that are controlled under the Barcelona Convention and other international agreements designed to prevent environmental damage.

In almost all sectors where PVC plastic is used, there are economical and safer alternatives. A move to PVC alternatives could take place with a minimum of harm to the industries which are involved, the workers and the community. For example, Petkim already manufactures plastics with less environmental problems than PVC, which, along with wood, textiles and other materials, would replace PVC in many applications. Increased demand for alternatives to PVC could help reduce the prices of the alternative products. It should also be remembered that the price we pay for a PVC product is a lot more when the environmental and health damages are considered.

In many countries, PVC use is becoming more restricted as its hazards are investigated and more fully understood. If the Turkish government is serious about its obligations under the Barcelona Convention, it should ratify all of the protocols and amendments of the Convention, formulate a large scale Clean Production programme for the industry in Turkey and phase out the production and use of PVC and other chlorinated substances.

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