BASEL CONVENTION TECHNICAL GUIDELINES ON HAZARDOUS WASTE FROM THE PRODUCTION AND USE OF ORGANIC SOLVENTS

Basel Convention on the Control of Transboundary Movements on Hazardous Wastes and Their Disposal

No. 6

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BASEL CONVENTION
ON THE CONTROL OF TRANSBOUNDARY MOVEMENTS OF
HAZARDOUS WASTES AND THEIR DISPOSAL

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SECRETARIAT

TECHNICAL GUIDELINES ON HAZARDOUS WASTE FROM THE PRODUCTION AND USE OF ORGANIC SOLVENTS (Y6)

These Technical Guidelines were prepared by the
Technical Working Group of the Basel Convention and
adopted by the second meeting of the Conference of the Parties
to the Basel Convention in March 1994, Geneva

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Technical Guidelines on Hazardous Waste from the Production and Use of Organic Solvents (Y6)

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Foreword

These technical guidelines are principally meant to provide guidance to countries who are building their capacity to manage waste in an environmentally sound and efficient way and in their development of detailed procedures or waste management plan or strategy. They should not be used in isolation by the competent authorities for consenting to or rejecting a transboundary movement of hazardous waste, as they are not sufficiently comprehensive for environmentally sound management of hazardous waste and other waste as defined by the Basel Convention. These technical guidelines concern waste generated nationally and disposed of at the national level as well as waste imported as a result of a transboundary movement, or arising from the treatment of imported wastes.

It is necessary to consider this document in conjunction with the Document on Guidance in developing national and/or regional strategies for the environmentally sound management of hazardous wastes (SBC Publication - Basel Convention Highlights No. 96/001 - December 1995) adopted by the second meeting of the Conference of the Parties. In particular, special attention should be given to the national/domestic legal framework and the responsibilities of the competent authorities.

These guidelines are meant to assist countries in their efforts to ensure, as far as practicable, the environmentally sound management of the wastes subject to the Basel Convention within the national territory and are not intended to promote transboundary movements of such wastes.

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INTRODUCTION

1. Many organic substances exhibit solvent type properties. Whilst any attempt to estimate the number in regular or common use involves subjective judgement, it is suggested that some 60 substances fall into this category. Annex 1 lists these substance, together with some information on their properties.

2. Solvents may be categorized in several ways, for example by industrial application, by chemical family, or by some property based description. The annex 2 shows groups of solvents by chemical type, or family.

3. Solvents display a very wide range of properties and characteristics. Many are flammable, some highly flammable, many are volatile and evaporate quite rapidly to give off vapours. Such vapours may be toxic or flammable-flammable vapours in confined spaces can be explosive. Toxic properties can be very varied, and include being carcinogenic, narcotic, ecotoxic and may even be mutagenic or teratogenic. Solvents may be more or less dense than water, more dense substances sinking to the bottom of watercourses, vessels etc. Whilst some solvents are totally miscible with water, others are not and display barely any solubility in water.

4. Solvents have three principal areas of use; as cleaning agents, as a raw material or feedstock in the production and manufacture of other substances, and as a carrying and/or dispersion medium in chemical synthetic processes. Users include many sectors of industry and commerce, not to mention some domestic applications. Particular industry user sectors are:

- Cleaning : Electronics, metal finishing, dry cleaning.
- Raw Material : Paints, resins, adhesives, plastics.
- Carrying Medium : Fire chemicals, pharmaceuticals, agrochemicals.

Wastes deriving from solvents and their use will often be classified as hazardous. Wastes cover a wide spectrum of composition and physical form – indeed, even wastes produced from the same plant or process may display considerable variations. Nevertheless, wastes are often considered as falling into some four categories.

- High solvent content: often relatively clean, derived from cleaning and washing processes.
- High organic content: solvents plus other reaction products and by products – from synthesis/manufacture of other substances
- Low organic content: highly aqueous wastes, from chemical processes, washing and extractions.
- Sludges and solid/ Semi-solid : manufacturing by products, recycling residues and residues from cleaning processes.

6. The use of solvents can lead, particularly in the case of more volatile substances, to comparatively high losses in use. These are often referred to as “fugitive” losses or emissions.

Options for Management of Wastes

7. Solvent wastes embrace a broad range of physical and chemical characteristics. The solvent part of the waste may constitute a large or small portion of the total. The balance may be solid or liquid material, and may consist of inert/semi-inert substances or other hazardous constituents of an organic or inorganic nature. Consequently, wastes may be highly mobile and pumpable at one extreme, or of a solid or virtually solid nature at the other.

8. The Strategic Priorities require that reasonable effort be made first to avoid or reduce the generation of he waste. Waste nevertheless generated should be dealt with via a suitable recovery option of practicable, and only if this cannot be achieved should disposal options be considered. Apart from the obvious consideration of relative cost, final choice will at least in part depend upon the quantity, physical and chemical nature of the waste, and possibly its form of packaging.

Waste Avoidance

9. The nature of solvents, and the uses to which solvents are consequently put, makes it unlikely that those uses can be avoided or eliminated altogether. However, substitution (see 10 below) and improved efficiencies of use, can effect the nature and quantity of waste, as can better separation of the components of waste streams at source. Such separation may avoid the creation of difficult mixtures, and result in separate streams more amenable to recovery/re-use.

10. Waste avoidance can be considered as including alterations to a process so that the waste generated is less dangerous an/or of reduced potential to harm the environment. Thus, waste avoidance may include the substitution of one solvent for another, where the use of a difficult or harmful solvent is avoided. Such practices are widely encountered in the projected phasing down of the use of chlorinated solvents, and are considered to have a major part to play in achieving real reductions in the potential for adverse environmental effects and overall environmental impact.

11. The avoidance of fugitive losses is a desirable objective in itself, but is unlikely to impact significantly on the quantity of waste requiring attention. It will however result in a reduced requirement for new material, and hence help reduce waste generation associated with the manufacturing process.

Waste Recovery

12. Although, the preferred option for dealing with solvent wastes is often regeneration and reclamation, via processes such as distillation, thin-film evaporation and steam stripping, often economic rather than technical considerations discourage this approach. This leads to their use as energy source/fuel.

13. The action of reclamation via a process such as distillation supposes that the original waste generator wishes to take back the clean material, or that some other equivalent or suitable outlet exist. Distillation and related processes are comparatively costly to carry out to

the standards of safety and environmental, care which should apply. They themselves generate wastes and residues, often in the form of distillation bottoms, the quantity and nature of which depend upon the original waste stream, but which must be disposed of with the utmost care – just as with any other waste.

14. In the simplest economic analysis, where not subjective value judgements are made as to the desirability of one option over another, and where no financial distortions are introduced, any decision to undertake recovery, reclamation or regeneration will be taken because it represents the lowest overall cost! (keeping in mind the necessity to avoid harming health and the environment). In estimating the "overall" cost care must be taken to include all the factors which can influence the balance of costs, so that comparisons of such costs are valid. For example, let us consider the case of a solvent waste taken to an external contractor for distillation, and then returned to the generator for re-use. Costs associated with this option would include:

- The contractor's distillation service fee, including his profit;
- The disposal of any residues from the distillation activity;
- Transport from, and return to the generator;
- Purchase by the generator of any new solvent to make up for losses inherent in the distillation process.

The total of these will represent the costs to the generator of recovering his waste so as to be able to continue with his commercial activity. His alternative would be to arrange for all the waste to be taken away for some form of disposal, and to purchase, new, all his ongoing solvent requirements. The cost of this alternative depends clearly on the particular solvent involved, and its consequent price, but also on the type of disposal. Disposal could, in some circumstances yield an income, such as whether the material is suitable for use as a fuel.

15. It follows that recycling and regeneration activities involving distillation and similar processes, tend to be favoured for high value solvents, the disposal of which is especially problematic and costly, or with large volumes arising of easily distilled solvent mixtures, particularly where this can be done at the point of productions, and the recovered product reused there.

16. Certain solvent wastes may be capable of use as a fuel, fuel substitute, or energy contributor to thermal processes. It is important to recognize that such applications need the most careful assessment, and the characteristics of the waste and the scope and capabilities of the process in which its combustion is proposed to take place, must be matched with care. It is likely there will be grater restrictions related to the use of halogenated solvents than for non halogenated ones. The ability to burn wastes in this way must not be regarded as an opportunity to dispose of wastes in a less technically sound manner, possibly at lower cost, than would otherwise be the case. Use of wastes in this way should be on the basis that emissions are set at, and controlled to a comparable level as would be required of an incinerator.

17. Examples of processes in which solvent waste may be used include energy intensive cement kilns and steam raising boiler systems. Such plants may not necessarily be equipped with the kinds of gas cleaning equipment needed to control emissions, nor would they always be provided with the control equipment, systems and procedures which specialist incinerators would usually employ. Nevertheless, subject to careful selection of waste streams such that emissions from these processes is not significantly adversely affected, there is no reason why appropriate wastes may not be beneficially utilized.

18. Use as a fuel can involve the injection and atomisation via conventional burner systems, the use of specialist burners such as ultrasonic units where dirtier but nevertheless mobile liquids are involved, or mixed with other substances in such a way as to allow the energy to be released. Use as a fuel will generally be confined to reasonably clean, mobile liquids, free of suspended materials, sludges or sediments, and having good calorific value. Sludges, and even solids can be sued beneficially in some circumstances, but where burner injection is not possible, other methods, although possible, are likely to be encountered much less frequently.

19. The essential pre-requisite for use as a fuel is that the solvent waste should burn reasonably well, have a good calorific value, and not contain hazardous constituents or elements which would lead to the generation of undesirable products of combustion, and emissions. Chlorine, fluorine, bromine, sulphur, nitrogen are elements frequently found in common solvents which will, upon combustion, generate substances which require careful control. As wastes, solvents may contain other substances such as potentially volatile metals, or thermally stable organic contaminants, all of which could lead to undesirable emissions or result in detrimental effect on the quality of a production such as cement in the absence of adequate control.

20. Halogenated solvents tend to have low calorific values, and waste streams containing high concentrations of such materials are unlikely to have value as fuel. Calorific values of waste stream will depend upon the composition of the stream, and the effect of other substances present.

Disposal Options

21. Solvent wastes not subjected to any recovery process, whether for lack of technical opportunity, or for economic reasons, must nevertheless be disposed of in a proper manner. Whilst incineration methods may well be the first to come to mind for such disposals, they are not the only ones available. Other possibilities may sometimes exist, although these alternative options are not equally appropriate or equally satisfactory in all circumstances. The options relevant for untreated solvent wastes and relating to the list of disposal methods set out Annex IV of the Basel Convention are:

- D3 Deep Injection
- D5 Specially Engineered Landfill
- D8 Biological Treatment
- D9 Physico-Chemical Treatment
- D10 Incineration on Land

These options only serve to identify the most common methods of disposal currently employed. They should not be interpreted as indicating preferred or possibly accepted methods for environmentally sound disposal of solvent wastes.

22. **Incineration** does provide the generally accepted disposal route for solvent wastes not being recovered. Incineration is a very flexible technique in that by judicious selection of incinerator design and of the various options for combustion gas cleaning, together with operating conditions selected for the purpose, a plant can be able to handle many types or combinations of waste. Incinerators may sometimes be constructed as part of a manufacturing process, to deal with the waste streams from that process. In such cases, the nature and composition of the wastes will usually be reasonably well defined, and the plan can be designed and constructed on the basis of a narrow scope of operation.

23. Some incinerators are operated on a service basis, providing a central focus of incineration capacity for a range of wastes and customers. Such plants may be operated by public authorities, by private companies, or by combinations of the two. The range and size of any particular 'contract' incineration operation is essentially a matter of balance, reflecting market size, the type of wastes to be handled, and the commercial basis on which the service is to be provided. A capacity to deal with a wide range of business may help generate a larger, and more stable operation, but the broader the range of business may help generate a larger, and more stable operation, but the broader the range of wastes, the more sophisticated will be the plant itself, and hence the more expensive. In practice, most of these multi-client, multi-waste, contract operations aim for maximum flexibility by providing the highest standards of equipment and facilities.

24. Wastes generated from solvent related activities embrace most of the range of physical and chemical variations. Simple, non-halogenated and essentially clean solvent waste is likely to be recovered, or at least used as a fuel. It is important to ensure that any incineration process has an adequate destruction efficiency and appropriate air emission controls. If for any reason incineration is considered necessary there must be a proper consideration of temperature, time, turbulence and excess oxygen. For example, minimum conditions of 850^{o}C[1], with gas-phase residence times of at least half a second will often suffice. Chlorinated solvents require more severe conditions, with many regulatory agencies specifying temperatures in the 1100oC-1200oC[2] range, and residence times of at least two seconds. Less mobile materials, such as sludges or viscous materials may require pre-treatment, blending with other wastes etc, or systems involving the use of special pumps and/or burners. Solid and semi-solid materials may require advanced handling and pre-treatment techniques such as maceration or shredding. Facilities exist for shredding solid waste in steel drums, reducing it to smaller fragments able to be introduced more easily to certain designs of incinerator. Incinerators taking solid hazardous wastes will usually be of the Rotary Kiln type, this representing current perceptions of 'State-of–the-Art'.

25. Hazardous waste incineration facilities may incorporate energy recovery as part of the combustion gas processing plant. Decisions whether or not to do so lie in commercial, technical and regulatory considerations. The presence of energy as part of an incineration system may not necessarily result in the system being classified as a recovery option.

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[1] Figures are given as examples.
[2] Figures are given as examples

26 **Landfill sites**, even when specially engineered to environmentally sound standards, and with advanced controls on leachate, gas generation etc, are not usually suitable for the disposal of solvent waste in bulk, particularly substances displaying high volatility, low flash points and auto ignition temperatures, malodour or significant toxicological hazard (associated with either the solvent itself, or contaminants present in it). Landfill may be appropriate for thick, semisolid or no-mobile solvent containing sludges, viscous or tarry solvent residues, minimal quantities in very small containers (incorporating elements of domestic and municipal refuse), laboratory scale wastes, and perhaps sometimes bulk aqueous waste containing low levels of organic solvents – depending upon the properties of the waste and the absorptive characteristics of the landfill site. Pre-treatment of these wastes, i.e. solidification may attenuate leachate problems. In all such cases, great care is needed and landfill site licenses and permits should be scrutinized to ensure that such activities are permitted.

27. **Biological methods** may the employed to degrade and dispose of certain solvent containing wastes, but great care and selectivity are required if such methods are to work effectively. These methods are generally more appropriate to essentially aqueous effluent streams in which certain solvents may be present, and are more likely to be installed at the locations generating the waste in question, or at least close enough to it for the waste to be moved there by pipeline.

28. Not all solvents are biodegradable (or at least, not at rates which are likely to be useful), and the biological process itself depends upon consistency and uniformity of the waste stream. Sharp fluctuations in the concentrations of biodegradable species, or changes in the species themselves, together with the presence of even very low concentrations of "poisons", can rapidly destroy the process activity. Many chlorinated solvents are quite unsuitable for conventional or current biological methods, either being resistant to break down, or "poisons" to the bio-system - or both!

29. **Physico-chemical treatment** methods exist which have at least the capability of dealing with certain types of solvent wastes. Processes such as Wet Air oxidation can be effective for aqueous wastes containing certain solvent species, whilst emerging technologies such as supercritical water are able to achieve high destruction efficiencies for aqueous wastes containing a broad range of organic species. Halogenated solvent wastes can, in theory at least, be processed via a range of chemical dechlorination processes but with most of these having been developed for persistent substances such as polychlorinated biphenyls, they cots rather more than is likely to be economically attractive at this time for chlorinated solvent wastes in general.

General Legislative Considerations for Waste Management

30. Most of the options considered for these wastes will involve transportation, whether to recovery facilities or disposal sites. Transportation of all dangerous goods requires care, and the observance of professional practices and standards as set out in various International Recommendations, Codes and Conventions (Guidance in Developing National and/or Regional Strategies for the Environmentally Sound Management of Hazardous Wastes – Basel Convention Highlights. No 96/001). Not all of these Codes and Conventions explicitly address the question of wastes, but they specify good practice and requirements of matters such as labelling, vehicle and package design, training of drivers, emergency information etc,

which are applicable to waste movements. Wastes are a sub-set of hazardous goods and require no measures beyond those needed for non-wastes of comparable properties.

31. All facilities and activities concerned with solvent wastes, whether they be recovery, transfer, storage or disposal sites, need to be operated under the provisions of a licence, permit, regulatory standard or other authorization system (Although this must be a subject for domestic legislation) which will specify the scope and manner of the activity. Issues which may be addressed include, the types and quantities of wastes to be processed, the methods of process proves employed and operating standards required, arrangements for record keeping, personnel numbers and qualifications, safety procedures and policies, insurance needs, monitoring and health screening. It is implied that the requirements will be monitored and enforced by the competent authority, which will have full access to all records.

32. The facility should be designed and constructed to appropriate standards. These should be at least sufficient to ensure that emissions and environmental releases of all kinds, and to all media are at levels consistent with the standards required to ensure protection of health and the environment.

Annex 1

LIST OF SOME COMMONLY USED SOLVENTS

	UN Class	UN Number	Flash Point (^oC)	Solution in Water (mg/kg)
Aliphatic Hydrocarbons				
- Cyclohexane	3	1145	-18	<1
- Naptha solvents	3	1256	<-20	<1
Aromatic Hydrocarbons				
- Benzene	3	1114	-11	0.2
- Toluene	3	1294	6	<1
- Xylenes	3	1307	25-30	<1
- Decahydronapthalene		1147		
Halogenated Hydrocarbons				
- Chloromethane	2	1063		
- Methylene chloride	6.1	1593	bd	1.3
- Chloroform	6.1	1888	nc	0.8
- Carbon tetrachloride	6.1	1846	nc	0.08
- 1, 1- dichloroethane	3	2362	-10	0.5
- Trichloroethylene	6.1	1710	bd	0.04
-1,1,1-trichloroethane	6.1	2831		
- Perchloroethylene	6.1	1897	nc	0.01
- Chlorobenzene	3	1134	29	<1
- o-Dichlorobenzene	6.1	1591	66	0
- p-Dichlorobenzene	6.1	1592		
- Ethylene dichloride	3	1184	13	<1
- Chloronitrobenzene	6.1	1578	127	0
- Ethyl Chloride	2	1037		
- Ethylene dibromide	6.1	1605	nc	<1
- Dichlorodiflourmethane	2	1028		
Alcohols, Glycols, Ethers, Phenols, Epoxides				
- Isobutanol	3	1212	28	
- Butanols	3	1120	35	
- 3-Pentanol	3	2706		
- Methanol	3	1230	11	100
- Ethylene glycol diethyl Ether	3	1153		
- Ethylene glycol monobutyl Ether	6.1	2369		
- Ethylene glycol monoethyl Ether acetate	3	1172		

	UN Class	UN Number	Flash Point (°C)	Solution in Water (mg/kg)
- Ethylene glycol Monoethyl ether	3	1188		
- Ethylene glycol methyl Ether acetate	3	1189		
- Dimethyl ether	2	1933		
- Propylene oxide	3	1280	-44	40
- Cresols	6.1	2076	81	2
- Phenol (molten)	6.1	2312	79	6.7
- Phenol (solid)	6.1	1671		
- Phenol (solutions)	6.1	2821		
- Isopropanol	3	1219		
- Ethanol	3	1170	12	100
Ketones, Aldehydes				
- Aldehydes, toxic	3	1988		
- Aldehydes, n.o.s.	3	1989		
- Formaldehyde (solutions)	9	2209		100
- Formaldehyde (solutions, inflammable)	3	1198	<23	
- Acetaldehyde	3	1089		
- Acetone	3	1090	-20	100
- Acrolein dimer, stabilized	3	2607		
- Acrolein, inhibited	3	1092	<-20	
- Methyl ethyl ketone	5.2	2563	-1	27
- Methyl ethyl ketone	5.2	2550		
- Methyln ethylene ketone	5.2	2127		
- Methyl isobutyl ketone	3	1245		
- Cyclohexanone	3	1915	43	6
- Diethyl ketone	3	1156		
Esters, Amides				
- Ethyl acetate	3	1173	-4	8.7
- Isobutyl acetate	3	1213	19	<<1
- Butyl acetate	3	1123	26	
- Methyl acetate		1231		24
Acids, Nitriles				
- Nitrobenzene	6.1	1662		<1
- Acrylonitrile	3	1093	-5	5

	UN Class	UN Number	Flash Point (^{o}C)	Solution in Water (mg/kg)
Heterocyclic Compounds				
- Tetrahydrofuran	3	2056	-17	100
- Furfural	3	199	60	8.3
Notes				
bd – burns with difficulty				
nc - noncombustible				

Source: OECD

Annex 2

SOME SOLVENT USES/WASTE GENERATION BY INDUSTRY

TYPE OF WASTE SOLVENTS	ARISINGS OF SOLVENT WASTES/ MAJOR USES OF
Acetone waste	Chemical industry, textiles, plastics, photographic, printing industry.
Acylonitride waste	Petrochemical industry.
Benzene waste	Cleaning and degreasing of metal.
Butanol waste	Chemical industry, pharmaceuticals, textile, manufacture of coatings.
Butyl acetate waste	Chemical industry, printing.
Carbon bisulfide waste	Chemical industry, textile industry, plastics processing.
Cyclohexanone waste	Chemical industry, textile, manufacture of coating plastics
Diethyl ether waste	Chemical industry, textile industry, plastics processing.
Dimethyl formamide waste	Chemical industry.
Dimethyl formamide waste	Chemical industry, textile, plastics.
Esters	Motor vehicle manufacture.
Ethanol waste	Chemical industry, therapeutic products, textile, extractive industry, printing, photographic.
Ethyl acetate waste	Chemical industry, manufacture of therapeutic and pyrotechnic products.
Glyco ether waste	Chemical industry.
Isopropanol	Extractive industries, food flavouring, cosmetics, toiletries, paint and varnish manufacture.

TYPE OF WASTE SOLVENTS	ARISINGS OF SOLVENT WASTES/ MAJOR USES OF
Kerosene waste	Cleaning and degreasing of metal, motor vehicle manufacture.
Methanol waste	Chemical industry, manufacture of therapeutic products.
Methyl ethyl ketone waste	Chemical industry, adhesives
Styrene waste	Petrochemical industry.
Tetrahydorfuran	Chemical industry, manufacture of therapeutic and pyrotechnic products.
Toluene	Cleaning and degreasing of metal, motor vehicle, adhesives, chemical industry.
Xylene waste	Cleaning and degreasing of metal, coking plants, gasworks, chemical industry, motor vehicle,printing industry.
Carbon tetrachloride waste	Plastics processing, chemical industry, manufacture of fluorocarbons, aerosol.
Chlorobenzene waste	Chemical industry, textile, dry cleaning, degreasing, manufacture of coatings.
Chloroform waste	Chemical industry, fluorocarbons, dyestuffs, pharmaceuticals, cosmetics, toiletries, textile, dry cleaning, degreasing, manufacture of coatings.
Dichloroethane waste	Chemical industry, vinyl chloride production, manufacture of paint, varnish and finish removers.
Ethyl chloride	Chemical industry, manufacture of tetramethyl lead.
Ethylene chloride waste	Chemical industry, textile, dry cleaning, degreasing, manufacture of coatings.
Ethylene dibromide	Chemical industry, synthetic resins, pesticides, anti-knock agent in fuels.
Methylene chloride waste	Chemical industry, pharmaceutical and food extraction, paint removers, degreasing.
Pentachlorophenol	Textile, wood, paint and biocide.
Perchlorethylene waste	Chemical industry, manufacture of fluorocarbons, textile industry, dry cleaning, degreasing.
111 trichloroethane	Wide range of solvent and degreasing applications, e.g. textile, rubber industry.
Trichloroethylene waste	Chemical industry, textile industry, dry cleaning, degreasing, manufacture of coatings.
Trichloroflouromethane	Aerosol, refrigerant, plastic foam blowing agent, chemical intermediate.

Source: OECD

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal was adopted in 1989 and entered into force in 1992. Presently, there are more than 150 Parties to the Basel Convention. Its objective is to protect human health and the environment from the adverse effects caused by the generation, management and transboundary movements of hazardous wastes.

The fundamental aims of the Basel Convention are the reduction of the transboundary movements of hazardous wastes, the prevention and minimization of their generation, the environmentally sound management of such wastes and the active promotion of the transfer and use of cleaner technologies.

In December 1999, the Parties to the Basel Convention adopted the Basel Protocol on Liability and Compensation for Damage resulting from the Transboundary Movements of Hazardous Wastes and Their Disposal.

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