







## CONFERENCE PAPER

### Application of Analytic Network Process (ANP) and PROMETHEE for different treatment/disposal technologies of persistent organic pollutants (POPs)

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## ABSTRACT

Persistent organic pollutants (POPs) are a group of hazardous chemicals that have persistent, bio accumulative and toxic properties regulated under Stockholm Convention (SC). This study was to a large extent focusing on selecting the appropriate treatment/disposal technologies for environmentally sound disposal of POPs in compliant with SC obligations. For this purpose, five different technologies were evaluated by Analytic Network Process (ANP) and PROMETHEE methods which are the most well-known Multi Criteria Decision Making (MCDM) methods. These technologies are incineration, base-catalyzed decomposition (BCD), gas phase chemical reduction (GPCR), pyrolysis/gasification and plasma arc. Eleven criteria by means of benefit, cost and risk were used for evaluation. Incineration was found as the preferred alternative for both methods (34 % for ANP and +0.41 for PROMETHEE). The second option for ANP and PROMETHEE was plasma arc (24%) and pyrolysis/gasification/ (+0.23), respectively. Although the results were slightly different for two options, this difference is due to the mathematical differences between the methods.

**Keywords:** ANP, MCDM, POPs disposal, PROMETHEE, treatment, waste

## 1. INTRODUCTION

Persistent Organic Pollutants (POPs) are globally concerned group of chemicals due to their resistant in nature, highly toxic properties including teratogenic, carcinogenic, endocrine disrupting effects and transboundary movement due to their semi-volatile characteristics [1]. POPs were used in several industrial processes and products. Even if the use of POPs is prohibited, it will continue to be in products and waste streams for many years. Furthermore, some treatment/disposal technologies can lead to the unintentional formation and release of POPs [2].

Several multilateral environmental agreements provide frameworks to prevent and minimize releases of toxic chemicals and hazardous wastes. The Basel, Stockholm and Rotterdam Conventions are a series of building blocks that dovetail to create a comprehensive life cycle approach to the management of hazardous chemicals and wastes. Together, these

conventions guide decision makers in their actions to minimize and manage the risks to the environment from a range of chemicals, products and wastes [3].

Provisions of the Stockholm Convention complement with the related articles for the management of hazardous wastes under the Basel Convention to form a comprehensive regime for managing POP wastes. These obligations coming from the two conventions are to be applied to POP wastes in making decisions about their Environmentally Sound Management (ESM) [4, 5]. ESM is a broad policy concept that is understood and implemented in various ways by different countries, stakeholders and organizations.

Within the abovementioned ESM framework, the following POPs destruction technologies, as provided in the Basel Convention, has been permitted for the destruction and irreversible transformation of the POP wastes when applied in a way that ensures the remaining wastes and releases do not present the characteristics of POPs:

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- (a) Alkali metal reduction
- (b) Advanced solid waste incineration (ASWI)
- (c) Base catalyzed decomposition (BCD)
- (d) Catalytic hydrodechlorination (CHD)
- (e) Cement kiln co-incineration
- (f) Gas phase chemical reduction (GPCR)
- (g) Hazardous waste incineration
- (h) Plasma arc
- (i) Plasma melting decomposition method (PMD)
- (j) Supercritical water oxidation (SCWO) and subcritical water oxidation
- (k) Thermal and metallurgical production of metals

Among these technologies, one technology can be in front of the other based on technical specifications or commercial availability in a country. In addition, different real-life parameters such as investment cost, pre-treatment option, distance, etc. can also affect the selection of proper disposal method in reality.

Multi-criteria decision making (MCDM) methods which has been used in this study are very commonly used in decision making studies. MCDM tools may be applied in many decision-making in problems for several environment related studies including waste management for either site selection or strategy development [6-10]. In the area of the study, MCDM tools were generally used for selection of the most suitable locations for establishment of waste management centers for municipal solid waste or other type of wastes. But studies used for either selection of site of determination of disposal/treatment strategy focuses mainly on municipal solid waste, recyclable waste, waste electrical and electronic equipment and medical waste. However, in some studies they were used for selection of appropriate technologies for medical waste treatment and wastewater treatment [11-13]. There are several tools that are used in MCDM studies such as target programming, Analytical Hierarchy Process (AHP), Analytical Network Process (ANP), Preference Ranking Organization Method for Enrichment Evaluations (PROMETHEE), TOPSIS and ELECTRE [14, 15]. In this study, ANP and PROMETHEE were selected as appropriate MCDM tools for assessment and comparison of POPs destruction technologies.

The ANP offers an approach to enter judgments and measurements to develop ratio scale priorities for the distribution of impact among the factors and groups of factors in the decision. Whereas the basic ANP structure consists of only one network, the most complex one can analyze the benefit, opportunity, cost and risk (BOCR) that each alternative can cause together. In ANP, to define the significance of the criteria and alternatives among each other, a pairwise comparison is conducted. In addition, comparison of alternatives is done for each criterion. To make a prioritization among the many objectives and many criteria, the judgments that are usually made in qualitative terms are expressed numerically. To do

this, rather than simply assigning a score out of a person's memory that appears reasonable, one must make reciprocal pairwise comparisons in a carefully designed scientific way. However, in case of a non-numeric criterion, it is used to assign a score that was developed by Saaty ranging from 1 to 9 [15].

PROMETHEE method was firstly developed by Brans in 1982 and it was extended in 1985 by Brans and Vincke [16]. In this method, data entries can be used directly without making any pairwise comparison. In order to implement PROMETHEE, two types of data are required that are relative significance of the criteria (weights) and values of alternatives according to criteria with respect to decision makers choice (function) [17]. The method accepts the decision maker's weighting as correct. The preference function in PROMETHEE, translates the difference between the evaluations of two alternatives into a preference degree ranging from 0 to 1 for each criterion [18]. There are 6 types of preference function that are usual, U-type, V-type, level, linear and Gaussian. For each criterion, a sensitivity threshold (q) if the function type is U-type; preference threshold (p) if the function is V-type or Gaussian; and both sensitivity and preference thresholds should be defined if the function is linear or level. There is no need for a threshold in usual preference function. PROMETHEE method consists of 5 steps. The procedure starts with determination of deviations from pair comparisons. Then, global preference index is calculated for each criterion by using the appropriate preference function (step 2 and 3). In step 4, positive and negative dominant flows are calculated for each alternative and partial ranking is conducted. In the final step, the procedure is completed by calculation of net dominant flow for each alternative and conducting a complete ranking [17, 18].

## 2. MATERIALS & METHODS

In this study two different MCDM methods were used: ANP and PROMETHEE. In both methods, the same alternatives and criteria were used for resolving the problem. The flowchart of the study was illustrated in Fig 1.

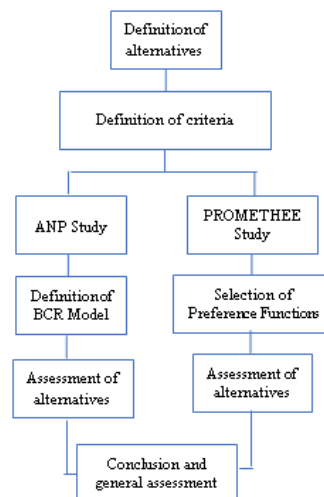


Fig 1. Flow chart of the study

## 2.1. Definition of Alternatives

The alternative technologies were selected according to the report prepared by Scientific and Technical Advisory Panel (STAP) of Global Environmental Facility (GEF) [16]. In this context, Incineration (A1), Base-Catalyzed Decomposition (BCD) (A2), Gas Phase Chemical Reduction (GPCR) (A3), Pyrolysis/Gasification (A4) and Plasma Arc (A5) were used as alternative technologies. These technologies were defined as commercial destruction/irreversible destruction technologies for POPs by GEF STAP.

## 2.2. Incineration (A1)

Hazardous waste incineration mainly uses flame combustion to treat organic contaminants, mostly in rotary kilns. The process typically involves heating to the temperature greater than 850°C or 1100°C (if the waste contains more than 1% of halogenated organic substances i.e. as chlorine) for a residence time greater than 2s under conditions that ensure appropriate mixing. Dedicated hazardous waste incinerators are available in a number of configurations, including rotary kiln incinerators and static ovens (for liquids with low contamination). High-efficiency boilers and lightweight aggregate kilns are also used for the co-incineration of hazardous wastes [2, 20].

## 2.3. Base-Catalyzed Decomposition (BCD) (A2)

The BCD process involves treatment of wastes in the presence of a reagent mixture consisting of a hydrogen-donor oil, an alkali metal hydroxide and a proprietary catalyst. When the mixture is heated to above 300 °C, it makes highly reactive atomic hydrogen that reacts with the waste to remove constituents that confer toxicity to the compounds [2, 21].

## 2.4. Gas Phase Chemical Reduction (GPCR) (A3)

The GPCR process involves the thermochemical reduction of organic compounds. At the temperatures greater than 850 °C and at low pressures, hydrogen reacts with chlorinated organic compounds to yield primarily methane, hydrogen chloride (if the waste is chlorinated), and minor amounts of low molecular weight hydrocarbons (benzene and ethylene). The hydrochloric acid is neutralized through the addition of caustic soda during the initial cooling of the process gas or can be taken off in acid form for reuse. The GPCR technology can be broken down into three basic unit operations: a front-end system (where the contaminants are transformed into a suitable form for destruction in the reactor), a reactor (which reduces the contaminants using hydrogen and steam), and a gas scrubbing and compression system [2, 21].

## 2.5. Pyrolysis/Gasification (A4)

Pyrolysis and gasification attempt to reduce the volume of waste by converting it into synthetic gas or oils, followed by combustion [19]. Gasification is a

pre-treatment/treatment technology for the recovery of hydrocarbon-containing waste which is operated at high temperatures and at high pressure using steam and pure oxygen in a reduced atmosphere. All hydrocarbon molecules in the waste are irreversibly decomposed to small gaseous molecules such as hydrogen (H<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). Short-chain hydrocarbons such as ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>) and other compounds are produced in small amounts (< 1 vol. %). Persistent organic pollutants including PCBs contained in the waste are effectively destroyed. The resulting raw gas is subsequently converted in a multistage process to pure synthesis gas for the production of highest-grade methanol [2, 23]. Pyrolysis is a similar approach which applies heat with no added oxygen in order to generate oils and/or syngas (as well as solid waste outputs) and requires more homogenous waste streams [19]. Different than Plasma Arc technologies, Pyrolysis/Gasification involve a plasma arc but destruction results from the heat generated by the arc, generally at lower temperature [19].

## 2.6. Plasma Arc (A5)

The waste in the form of liquid or gas, is injected directly into the plasma and is rapidly (<1 ms) heat up to about 3100°C and pyrolyzed for about 20 ms in the water-cooled reaction chamber (flight tube). The high temperature causes compounds to dissociate into their elemental ions and atoms. Recombination occurs in a cooler area of the reaction chamber, followed by a quench, resulting in the formation of simple molecules. The plasma arc system requires a mono-nitrogen oxides (NO<sub>x</sub>) abatement device, as important amounts of NO<sub>x</sub> are produced by the high temperature flame [2, 21].

## 2.7. Definition of Criteria

In this study, the following criteria listed in Table 1 was used for both ANP and PROMETHEE methods. In addition, in "benefit, opportunity, cost and risk" analysis of ANP method, benefit and opportunity clusters were combined and "benefit, cost and risk" analysis was conducted.

## 2.8. ANP Study

In order to assess the most suitable POPs treatment/disposal technology via ANP method, Super Decision software was used. For this purpose, a benefit, cost and risk analysis were conducted according to performance values listed in Table 2. For criteria between g4-g8, direct data was entered but for the rest scoring method through pairwise comparison was applied. It was pointed out that the inconsistency ratios were less than 10% due to the nature of the method [21].

The significance of the weighting of the chosen criteria was formulated in the program as additive (reciprocal):

Formula:

$$bB + oO + c(1/C) + r(1/R) \text{ with } r = 1/2; c = 1/3; b = 1/6; \text{ and } o = 0 \quad (1)$$

where B is Benefit, O is Opportunity, C is Cost and R is Risk.

In this context, first each cluster is rated separately. Then, these ratings are combined using the cluster weighting and the formulas including that to multiply the benefit ratios, reciprocals of cost and risk ratios. Finally, these raw results are normalized, and the values can be used as percentages for the evaluation of the alternatives [25].

**Table 1.** Criteria used in ANP and PROMETHEE methods

No	Name	Unit/Score	Remarks
<b>Benefit Cluster (for ANP)</b>			
g1	Disposal time	Day, decreasing	Number of days for disposal of same amount of POPs waste
g2	Chemical usage	Score (1-9), decreasing	Amount of chemicals added to process for disposal of same amount of POPs waste
g3	Easy application	Score (1-9), increasing	Complexity and difficultness of the application
g4	Destruction Efficiency (DE)	%, decreasing	Destruction performance of the method
g5	Destruction and Removal Efficiency (DRE)	%, decreasing	Destruction and removal performance of the method
<b>Cost Cluster (for ANP)</b>			
g6	Operation cost	\$/ton, decreasing	Amount of operation cost including energy, water, labor cost for disposal of same amount of POPs waste
g7	Preparation cost	\$/ton, decreasing	Amount of preparation cost for disposal of same amount of POPs waste
g8	Capital cost	\$/ton, decreasing	Amount of investment cost including infrastructure and equipment for disposal of same amount of POPs waste
<b>Risk Cluster (for ANP)</b>			
g9	Effective distance	m, decreasing	Distance of waste to the facility
g10	Climate conditions	Score (1-9), increasing	Influence of climate on the method
g11	Waste/Emission generation	Score (1-9), decreasing	Amount of waste/emission generated during the disposal of the same amount of waste

**Table 2.** Performance values of criteria

No	A1	A2	A3	A4	A5
g1	2	8	7	6	6
g2	3	7	8	3	2
g3	1	4	8	6	8
g4	99.999	99.9999	99.9999	99.974	99.9999
g5	99.9999	99.9999	99.9999	99.9999	n.a.
g6	1000	1500	1200	900	2000
g7	100	400	300	250	300
g8	10	2-3	7-9	12	12
g9	2	5	6	3	8
g10	1	9	9	1	1
g11	3	6	5	3	2

**2.9. PROMETHEE Study**

In application of PROMETHEE method, academic version of D-Sight software was used. Assessment was conducted with the data given in Table 2. Usual preference function was used in the criteria that has

numeric values, the most appropriate and common Gauss function, and that has scoring values (1-9). Criteria properties and weights were provided in Table 3. Sum of the weighting values is equal to 1 and the most dominant cluster of criteria was risk cluster.

**Table 3.** Criteria properties and weights for PROMETHEE

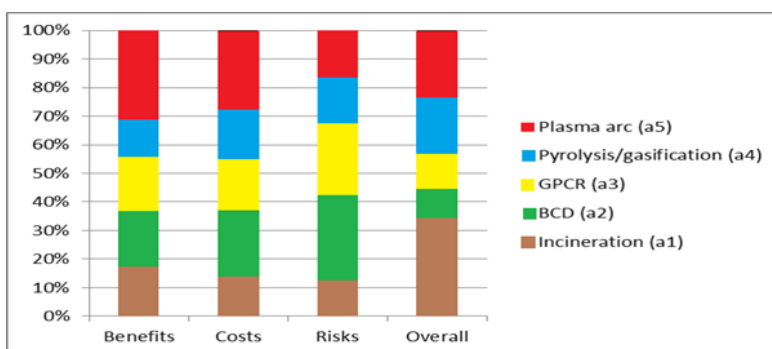
Criteria	Minimum/Maximum	Function Type	Absolute/Relative	Weights	Unit
g1	Minimum	Usual	Relative	1.6	1-9
g2	Minimum	Usual	Relative	0.5	1-9
g3	Maximum	Usual	Relative	1.2	1-9
g4	Maximum	Gauss	Absolute	6.8	%
g5	Maximum	Gauss	Absolute	6.5	%
g6	Minimum	Gauss	Absolute	20.4	\$ ton <sup>-1</sup>
g7	Minimum	Gauss	Absolute	9.0	\$ ton <sup>-1</sup>
g8	Minimum	Gauss	Absolute	3.9	\$ ton <sup>-1</sup>
g9	Minimum	Usual	Relative	14.3	1-9
g10	Minimum	Usual	Relative	3.1	1-9
g11	Minimum	Usual	Relative	32.6	1-9

**3. RESULTS & DISCUSSION**

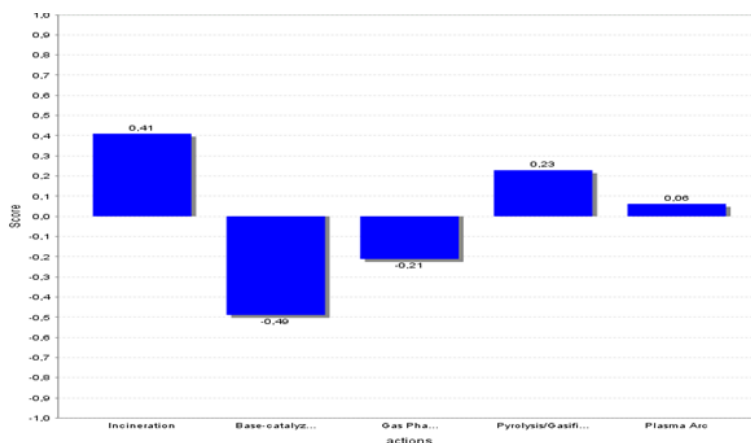
The alternatives for choosing the most appropriate technology for environmentally sound treatment/disposal of POPs wastes were evaluated with ANP and PROMETHEE methods. The results of ANP method in terms of benefit, cost and risk were given in Fig 2 in addition to aggregated results of clusters. According to the figure, the most appropriate alternative for benefits is plasma arc whereas the incineration is the most appropriate one for the cost and risk. On the other hand, overall results which aggregated based on the weight of clusters show that

incineration should be the most preferable technology for destruction of POPs.

The preference ranking of alternatives obtained by PROMETHEE method is presented in Fig3. In this figure, highest positive score shows the most appropriate alternative. In this context, incineration (a1) is the most preferable method and followed by pyrolysis/gasification. Despite its positive value, plasma arc (a5) has relatively lower score compared to incineration and pyrolysis/gasification. On the other hand, base-catalyzed decomposition (BCD) (a2) and gas phase chemical reduction (a3) has negative scores that shows their non-compliance.



**Fig 2.** ANP results in terms of benefit, cost, risk and overall



**Fig 3.** Ranking of alternatives with PROMETHEE

Results obtained in both MCDM methods were compared in Table 4. In both methods, incineration is the most appropriate technology for environmentally sound treatment/disposal of POPs wastes. BCD and GPCR take place in the same order in both methods. On the other hand, the plasma arc is the second in ANP- the third in PROMETHEE and vice versa for pyrolysis/gasification. While considering the most criteria for these two alternatives are relatively close to each other this kind of a shift might be reasonable expected.

**Table 4.** Comparison results of POPs treatment/disposal technologies with ANP and PROMETHEE

Alternatives	Ranking	
	ANP	PROMETHEE
Incineration (a1)	1	1
Base-catalyzed decomposition (BCD) (a2)	5	5
Gas Phase Chemical Reduction (GPCR) (a3)	4	4
Pyrolysis/Gasification (a4)	3	2
Plasma Arc (a5)	2	3

#### 4. CONCLUSIONS

Several commercial/near commercial technologies are available for environmentally sound disposal/destruction of POPs. However, due to availability and pollution specific circumstances different technologies can be accepted as more appropriate than others for all kinds of POPs treatment/disposal activities in a country. Technical (Destruction Efficiency, Destruction and Removal Efficiency, waste release/emission, chemical usage, etc.) and economical (operation costs, preparation costs, capital costs, etc.) criteria should be considered to choose a technology. At this point, MCDM methods help to decision makers for strategic planning of similar problems. However, there is not a wide usage of MCDM tools for determination of appropriate disposal/treatment technologies for hazardous wastes such as POPs. In the present study, ANP and PROMETHEE were used to decide which

treatment/disposal technology best fits for POPs. It is thought that this study may serve as an example for different countries. According to the evaluations using both techniques, incineration was found to be the most appropriate option for treatment of POPs in Turkey. Since there is about 10% difference from the next alternatives in the ranking, it can be said that the result is robust. The main factors influencing this result were low cost and risk. Policies for dissemination of POPs disposal/treatment technologies among the country should consider these parameters and the results.

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