



Method for the Effective Neutralization of Organochlorine Pesticide Waste – Selected Examples

Jolanta Biegańska^{1*}, Andrzej Biessikirski², Mariam Avagyan³, Kristine Sahakyan⁴

¹Department of Hydrogen Energy, Faculty of Energy and Fuels, AGH University of Krakow, Poland

<https://orcid.org/0000-0003-2356-3247>

²Department of Mining Engineering and Occupational Safety, Faculty of Civil Engineering and Resource Management, AGH University of Krakow, Poland

<https://orcid.org/0000-0002-2023-6454>

³Faculty of Urban Economy and Ecology, National University of Architecture and Construction of Armenia, Yerevan, Republic of Armenia

<https://orcid.org/0009-0008-2807-7583>

⁴Faculty of Urban Economy and Ecology, National University of Architecture and Construction of Armenia, Yerevan, Republic of Armenia

<https://orcid.org/0000-0003-4639-4837>

*corresponding author's e-mail: biega@agh.edu.pl

Abstract: This article reviews conventional methods for the disposal (neutralization) of waste pesticides belonging to the POPs group and demonstrates their effectiveness. Organochlorine pesticides from this group were characterized, with particular emphasis on their impact on human health and the environment. An unconventional disposal method was also presented, highlighting its advantages. While discussing the types of explosives used in mining, the possibility of modifying them for this purpose was noted. Using a selected organochlorine pesticide as an example, the effectiveness of its decomposition by the detonation method was demonstrated. The potential application of this method for the disposal of organochlorine pesticide waste under industrial limestone mining conditions was also discussed.

Keywords: waste organochlorine pesticides (POPs), neutralization, detonation combustion, explosives

1. Introduction

Pesticide waste is the result of improper management and handling of chemical substances commonly used in many types of agricultural crops. The purpose of using such agents is to control pests, weeds, and plant diseases, primarily for crop protection. Pesticides have also been used to combat diseases affecting humans (e.g., malaria and epidemic typhus) transmitted by parasites in certain regions of the world (Khan et al., 2023; Bailey, 2022; Bouwman et al., 2011). Excessive stockpiling and overproduction generate waste that, in the case of these substances, poses a threat to both human health and the environment.

The problem of pesticide waste affects many countries, particularly those undergoing political and economic transformation. One example is Armenia, a post-Soviet republic where agriculture is a major source of income for the rural population. Agricultural activities occupy approximately 44% of the Republic's territory, with a total area of 29,743 km² (Statistical Committee, 2020).

Since the 1950s, pesticides have been widely used for about 30 years (Dvorská et al., 2012; Sargsyan & Sargsyan, 2006) in connection with intensive food production, which also generated waste. In addition, stocks of expired toxic substances accumulated and were stored at 10,000 locations across the former Soviet Union, the southern Balkans, and the new member states of the European Union (Simeonov et al., 2013; Vijgen & Egenhofer, 2009). After many years, the storage of such pesticides resulted in negative environmental impacts, contaminating soil, irrigation water, and agricultural crops (Hovhannisyanyan et al., 2019). In Armenia, there was no official disposal site for obsolete pesticides; most waste was stored in facilities or disposed of in an unorganized manner (Speranska (Сперанская), 2004).

The largest stockpiles of obsolete pesticides were accumulated at the Nubarashen municipal landfill in Yerevan, while other quantities were dispersed throughout the country. According to estimates (Tauw, 2014), the total amount of toxic waste at this site reached 1,052 tonnes, while more than 4,000 tonnes consisted of contaminated soil. Other data (FAO 2021) indicate that 1,200 tonnes of these substances were accumulated (including 900 tonnes of banned pesticides), whereas soil contaminated with hazardous substances amounted to 12,650 tonnes (4,150 tonnes contaminated with second-category hazardous waste and 8,500 tonnes classified as third-category hazardous waste). The most recent sources (UNECE 2024) report that the landfill currently contains 1,250 tonnes of chemical waste, including so-called "Persistent Organic Pollutants" (POPs),



such as organochlorine pesticides. Qualitative and quantitative analyses of soil samples collected near the landfill (Avagyan, 2016; Avagyan, 2019) revealed high concentrations of POPs exceeding permissible standards. Among the identified substances, DDT and its metabolites, as well as heptachlor, were detected.

2. Characteristics of Organochlorine Pesticides

Persistent Organic Pollutants (POPs) exhibit toxic properties and are resistant to degradation. They are capable of long-range transboundary transport and deposition in remote locations, and they accumulate in terrestrial and aquatic ecosystems. These compounds are highly persistent and physicochemically stable (Jayaraj et al., 2016; Aktar et al., 2009). They are insoluble in water but highly soluble in fats, which causes them to accumulate in adipose tissues, negatively affecting humans and other organisms (Ortiz-Hernández et al., 2013). Exposure to POPs (through consumption of contaminated food and water, dermal contact, or inhalation) leads to chronic diseases, developmental defects in children, and may result in death (Zacharia, 2019; Thakur & Pathania, 2020; WHO, 2010; Roberts, James & Karr Catherine, 2012; Dewan et al., 2013).

The classification of POPs distinguishes (Anwar et al., 2018) three sources of their origin (Fig. 1):

1. **Typical pesticide sources** (natural and synthetic): aldrin ($C_{12}H_8Cl_6$), chlordane ($C_{10}H_6Cl_8$), dichlorodiphenyltrichloroethane (DDT) ($C_{14}H_9Cl_5O$), dieldrin ($C_{12}H_8Cl_6O$), endrin ($C_{12}H_8Cl_6O$), hexachlorobenzene (HCB) (C_6Cl_6), hexachlorocyclohexane (HCH) ($C_6H_6Cl_6$) and its isomers (α -HCH, β -HCH, γ -HCH), heptachlor ($C_{10}H_5Cl_7$), mirex ($C_{10}Cl_{12}$), and toxaphene ($C_{10}H_{22}Cl_8$). These substances constitute the so-called "dirty dozen" or "forbidden dozen".
2. **Industrial sector products**, including: polychlorinated dibenzo-p-dioxins (PCDDs) ($C_{12}H_{8-n}Cl_nO_2$, where $n = 1-8$) and polychlorinated dibenzofurans (PCDFs) ($C_{12}H_{8-n}Cl_nO$, where $n = 1-8$); the general term "dioxins and furans" is often used. The most toxic forms are 2,3,7,8-PCDDs ($C_{12}H_4Cl_4O_2$) and 2,3,7,8-PCDFs ($C_{12}H_4Cl_4O$).
3. **Unintentional releases as by-products**: polychlorinated biphenyls (PCBs) ($C_{12}H_{10-n}Cl_n$, where $n = 1-10$).

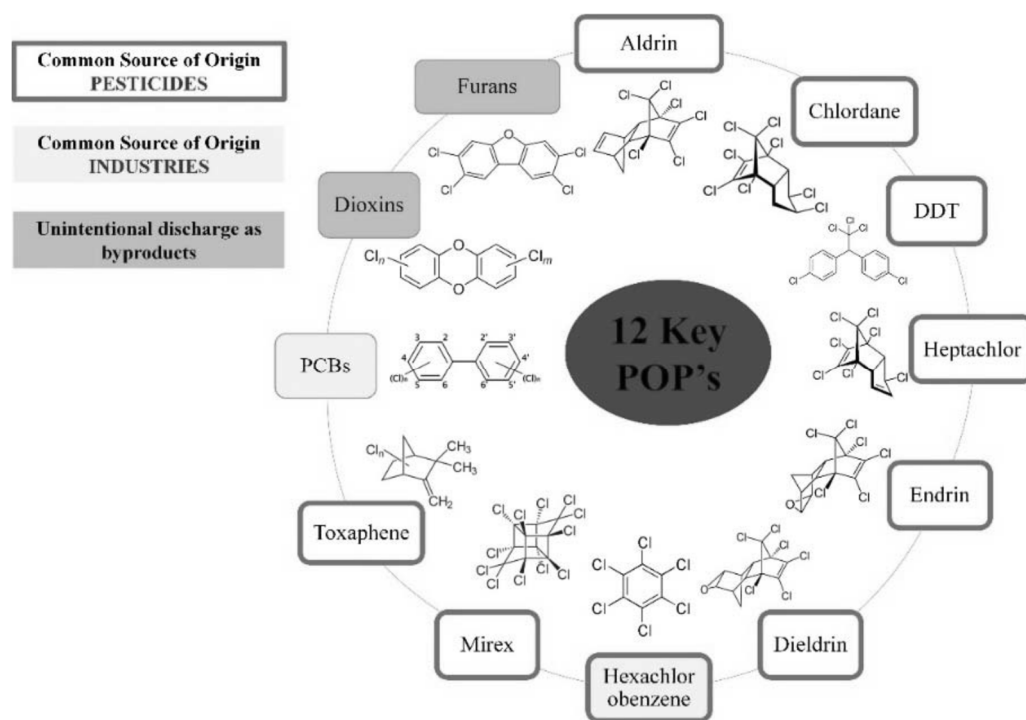


Fig. 1. Major persistent organic pollutants and their primary sources (Anwar et al. 2018)

A more recent classification of POPs (Aravind Kumar et al. 2022) also distinguishes three groups divided into:

1. **Hydrocarbons**: benzene (C_6H_6), toluene ($C_6H_5CH_3$), ethylbenzene ($C_6H_5CH_2CH_3$), xylene (BTX) ($C_6H_4(CH_3)_2$), and polycyclic aromatic hydrocarbons (PAHs) (C_xH_y , where $y < x$).
2. **Industrial chemicals**: polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs).
3. **Pesticides**: aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene, hexachlorobenzene, and dichlorodiphenyltrichloroethane (DDT).

The substances listed above are mainly organochlorine compounds. They are characterized by high environmental persistence (which increases with the number of chlorine atoms) and possess long half-lives (DT50) in soil and sediments, ranging from 60 days to 12 years (Zhu et al., 2005; Benimeli et al., 2008; Joseph et al., 2020; Syafrudin et al., 2021). Due to their properties, harmful effects, and widespread use in developing Asian countries (Lallas, 2001; Gupta, 2004; FAO, 2005), the Stockholm Convention (UNEP, 2010) decided to restrict or eliminate the production and use of these 12 POPs (the "dirty dozen").

3. Conventional Methods for the Disposal (Neutralization) of Pesticide Waste

Obsolete pesticides withdrawn from use (waste pesticides) should be disposed of safely. The disposal method should not pose a threat to human health nor negatively affect the environment. It is essential to apply processes that decompose the biologically active substance (the active ingredient responsible for the pesticide's actual properties), resulting in a new compound that does not pose an environmental hazard.

A disposal method is selected individually for each type or group of pesticides with a similar chemical structure. Biological, physical, chemical, and thermal methods have been developed. For selected organochlorine pesticides, the most effective and efficient destruction (transformation) methods were proposed in (BCRC-Caribbean, 2020) (Table 1). Methods for pesticides such as dieldrin, mirex, and toxaphene, which belong to the so-called "dirty dozen", were also considered (Sadiq et al., 2025).

Table 1. Methods for the destruction and irreversible transformation of selected POP pesticides, including their potential application for waste pesticides (Ministry of the Environment, 2004; Butler et al., 1981)

Technology	Aldrin	Chlordane	DDT	Dieldrin	Endrin	Heptachlor	HCB	HCH	Mirex	Toxaphene
Alkali metal reduction	-	+	-	X	-	-	-	+	X	X
Base-catalysed decomposition	-	X	X	X	-	-	X	X	-	X
Cement kiln co-incineration	X	X	X	X	X	X	X	X	X	X
Gas phase chemical reduction	X	X	X	X	X	X	X	X	X	X
Hazardous waste incineration	X	X	X	X	X	X	X	X	X	X
Plasma arc	-	X	X	X	-	X	X	-	X	X
Supercritical water oxidation and subcritical water oxidation	-	X	X	X	-	-	-	-	X	X

POPs destruction and transformation technologies are evaluated using two parameters:

1. **Destruction Efficiency (DE)** – defining the fraction of a given contaminant (e.g., Persistent Organic Pollutants, POPs) that has been effectively decomposed during the neutralization process.
2. **Destruction and Removal Efficiency (DRE)** – defining how efficiently a given process (typically combustion or thermal treatment) eliminates specific hazardous substances from waste streams.

The values of these parameters for the technologies listed in Table 1 are close to 100%. For example:

- **Alkali metal reduction** achieved a DE of 99.999% and a DRE of 99.9999% for chlordane and HCH (Sadiq et al. 2025).
- **Base-catalysed decomposition** achieved identical values for the above-mentioned POPs (UNEP 2001).
- **Cement kiln co-incineration** of DDT resulted in reported DE values ranging from 99.9335% to 99.9998%, while DRE exceeded 99.9999% (Yan et al., 2014; Li et al., 2012; Danish Environmental, 2004; Karstensen, 2001; Stobiecki et al., 2001).
- **Gas-phase chemical reduction** for DDT and HCB demonstrated DRE values of 99.9999% (Kümmeling et al., 2001; UNEP, 2004; Vijgen, 2002).
- **Hazardous waste incineration** achieved DE values exceeding 99.999% and DRE values exceeding 99.9999% for aldrin, endrin, HCH, and DDT (Ministry of the Environment, 2004).

- **Plasma arc technology** enabled contaminant removal efficiencies of up to 99.9999% for most pesticides from the above-mentioned group, including chlordane, DDT, and heptachlor (Yan et al., 2014; Vijgen, 2002).
- **Supercritical water oxidation** and **subcritical water oxidation** were characterized by exceptionally high efficiency values for chlordane and DDT:
 - in the case of **supercritical water oxidation**, DE exceeded 99.999%, and DRE exceeded 99.9999%,
 - whereas **subcritical water oxidation** achieved DE values above 99.999999% and DRE values above 99.999999% (UNEP, 2001; Vijgen, 2002).

The above-mentioned technologies proved to be exceptionally effective, particularly for selected pesticides. High-temperature processes or those conducted under extreme conditions (e.g., subcritical water oxidation) demonstrated the highest efficiencies.

For the disposal of toxic waste accumulated at the Nubarashen landfill in Armenia, high-temperature incineration and the potential application of supercritical water oxidation technology were proposed (Avagyan, 2024).

Combustion processes are considered a radical method of waste neutralization because they enable the decomposition of organic compounds, biological sterilization, and a significant reduction in waste volume. For many years, Polish legislation (Regulation of the Minister of Development, 1981) recommended this approach for the treatment of numerous categories of hazardous waste.

The Regulation of the Minister of Development of January 21, 2016, on requirements for the thermal treatment of waste and methods for handling waste generated by the process (Journal of Laws 2016, item 108) is currently in force. Hazardous waste (including pesticides) containing more than 1% of organochlorine compounds, calculated as chlorine, must be incinerated at a temperature of at least 1100°C.

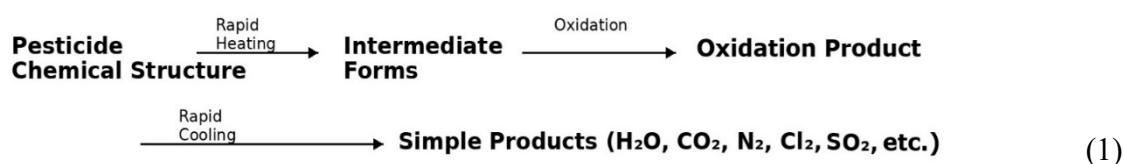
A major issue associated with gaseous emissions from combustion processes is the formation of PCDDs and PCDFs, which are POPs, under unfavorable operating conditions. These compounds may form (Wielgosiński, 2019) in incinerator flue gases within the flue gas cooling zone (de novo synthesis) or under improper combustion conditions, such as insufficient oxygen supply.

4. Unconventional Method for the Neutralization of Pesticide Waste

Despite numerous studies devoted to neutralizing particularly hazardous waste, including organochlorine pesticides, no universal technology has yet been developed. Most commonly, specific methods are proposed either for a particular group of compounds or for individual substances. It has been observed that processes conducted under high-temperature and high-pressure conditions enable the effective destruction of hazardous substances.

Studies and computer simulations on the decomposition of pesticides belonging to different chemical groups under extreme conditions have been conducted (Biegańska 2003, 2005, 2007, 2011; Biegańska et al., 2013; Biegańska, 2013; Biegańska & Barański, 2022; Biegańska et al., 2025; Biegańska, 2025). Such conditions occur during the detonation of high-energy materials (explosives).

The decomposition of pesticides under such conditions is possible when a mixture of the pesticide and the explosive material is prepared. The extremely rapid decomposition reaction leads to the formation of substances commonly occurring in nature (H₂O, CO₂, N₂, etc.), while the expected decomposition mechanism may be described by the following equation:



At elevated temperatures, the chemical compound undergoes destruction, followed by oxidation and rapid cooling of the resulting products. The very high reaction rates and temperatures prevent recombination processes that could otherwise lead to the formation of compounds with greater thermodynamic stability. The selection of explosive components affecting the composition of detonation products is based on determining the elemental oxygen balance, commonly referred to in explosive technology as the oxygen balance (Fickett & Davis, 2000). This parameter defines the oxygen content in the explosive relative to the amount of oxygen

theoretically required for complete oxidation of the combustible elements present in the formulation (e.g., carbon to CO₂, hydrogen to H₂O, etc.). An excess or deficiency of oxygen (positive or negative oxygen balance) during explosive detonation results in the formation of toxic oxides such as nitric oxide (NO), nitrogen dioxide (NO₂), and carbon monoxide (CO) (Sobala & Świetlik, 1991; Sobala & Rosmus, 1996; Biessikirski et al., 2020; Mainiero et al., 2006; Onederra et al., 2012; Zawadzka-Małota, 2015). Mining regulations permit the presence of the above-mentioned oxides in post-blast gases generated by explosives used in underground mining operations at concentrations not exceeding: CO = max. 0.135% and NO = max. 0.080%.

Even a properly designed explosive composition combined with appropriately conducted blasting techniques does not guarantee the complete elimination of toxic compounds. Due to their chemical composition, some explosives produce additional compounds in their detonation products (Sinabell, 1960; Buczkowski & Pałowski, 1996; Trębiński & Trzciński, 1999), including CH₄, C₂H₂, HCN, and others. In mining practice, these compounds are not regulated by legislation.

5. Explosives Used in Mining

Mining constitutes an important component of the industrial sector. Natural resource deposits are fundamental to the global economy. Armenia has historically relied heavily on the mining industry due to its significant deposits of copper, gold, precious stones, molybdenum, lead, silver, and zinc (World Bank, 2016). Currently, more than 670 solid mineral deposits with confirmed reserves are located within the country, including 30 metal ore deposits (Ministry of Energy, 2021). Approximately 400 deposits are under exploitation, including 22 metal deposits containing copper, molybdenum, gold, and iron ores.

The extraction of natural resources is fundamentally dependent on the use of explosives. The practical applicability of explosives is determined by typical parameters such as explosive performance, operational safety during blasting works, and economic efficiency; however, increasing emphasis is also placed on environmental protection aspects (Biegańska, 2001, 2002). Explosives designed to ensure minimal toxicity of post-blast gases have been developed. In Poland, particularly in surface mining operations, ammonium nitrate(V)-based explosives (NH₄NO₃) are widely used, including ANFO (ammonium nitrate/fuel oil) and emulsion explosives, which consist of multiple components integrated into a matrix structure (Maranda et al., 2001).

The principal explosives used in the Armenian mining industry include:

1. **Ammonite 6ZhV (cartridged explosive)** (АММОНИТ 6ЖВ) – intended for blasting operations involving manual loading of dry or dewatered blast holes or boreholes in all climatic zones of Russia (primarily applied in underground mining operations). This explosive contains: waterproof ammonium nitrate (GOST 14702-79) at 79.0 ± 1.5% and TNT (GOST 4117-78) at 21.0 ± 1.5%.
2. **Granulated Igdanite** (Гранулит Игданит) – intended for blasting operations involving mechanized loading of dry or dewatered blast holes, boreholes, and chambers under all climatic conditions (mainly used in surface mining). Igdanite consists of: ammonium nitrate(V) at 94.5 ± 0.5% and diesel fuel at 5.5 ± 0.5%.

The Polish equivalent of Igdanite is ANFO, composed of 94% ammonium nitrate(V) (porous ammonium nitrate) and 6.0% diesel fuel.

Due to its binary composition and ease of modification, this type of explosive may constitute a suitable basis for application in the neutralization (disposal) of pesticide waste.

6. Example of Pesticide Waste Disposal Using Explosives

A typical representative of the organochlorine pesticide group is DDT. Its structural analogue is the insecticide methoxychlor (Fig. 2), the disposal of which was investigated experimentally (Biegańska, 2013) using ANFO-based explosives.

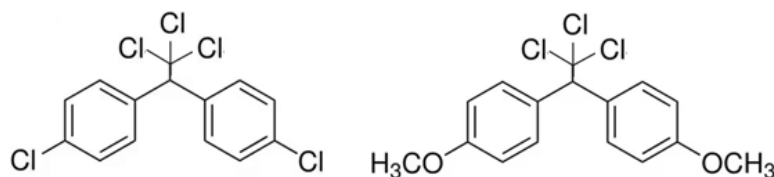
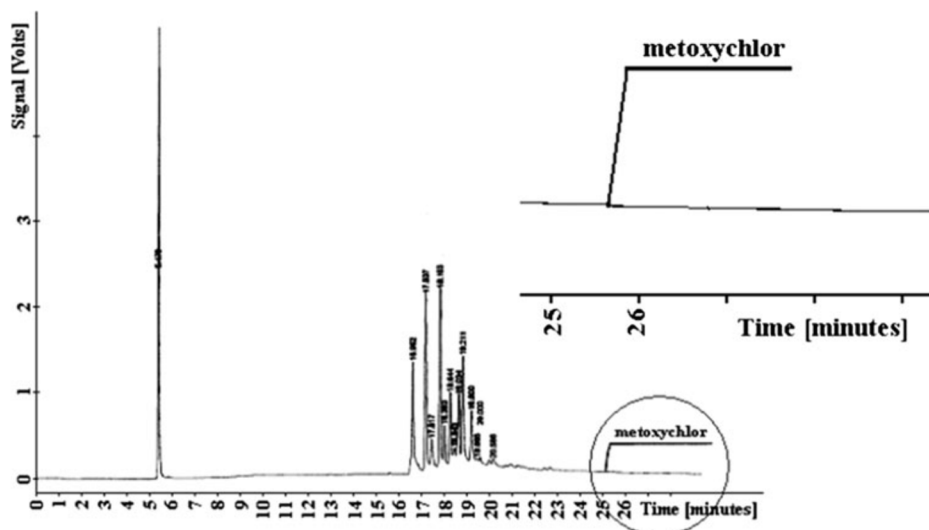


Fig. 2. Chemical structures of DDT and methoxychlor (Blum et al., 2008)

Detonative decomposition experiments for methoxychlor were conducted (Biegańska, 2003) using a modified ANFO-type explosive formulated under the assumption of zero oxygen balance (for an oil content ($C_{17}H_{36}$) of 5.47% in the explosive composition) and a density of $d = 0.900 \text{ kg/dm}^3$. The prepared mixture consisted of 89.67% NH_4NO_3 and 10.33% methoxychlor.

The experimental procedure, including calculations, blast-hole design, preparation of explosive charges, and sample collection, was similar to that described by Biegańska (2005) for the decomposition of DNOC in soil. The amount of pesticide remaining in the extracted samples was determined using gas chromatography with a Varian 3400 gas chromatograph. Methoxychlor eluted at a retention time of $t_R = 25.572$. The chromatogram of the residual component, with the retention parameter marked on the diagram, is presented in Fig. 3.



The calcium carbonate produced during detonation is calcined in rotary kilns, which provides an additional safeguard against the destruction of trace amounts of pesticides that might remain in the rock in the event of errors during blasting operations.

The authors believe that, given current environmental regulations, the most appropriate method for the disposal or neutralization of organochlorine pesticide waste is high-temperature incineration under controlled conditions. The proposed detonation combustion offers such possibilities, since temperatures in this process exceed 2,000°C.

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