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The Hidden Danger of Organic Phosphates

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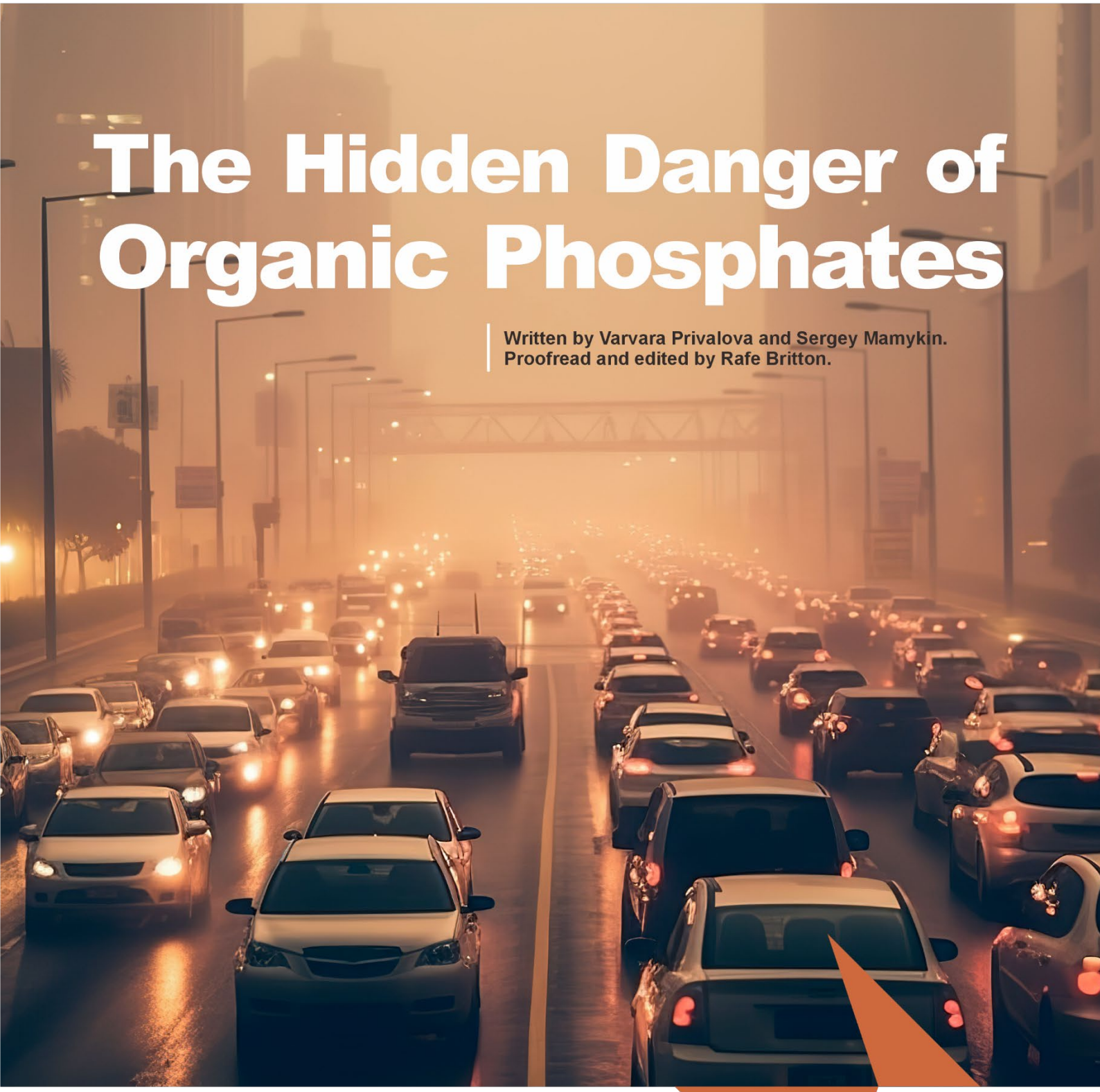


Organophosphates (OPs/OPEs), or organic phosphates, are a family of chemicals that contain a phosphate group, bound to either sulphur or oxygen by a double covalent bond [2]. Their general structure can be written as S/O=P(OR)3. OPs are created during esterification between sulphuric acid and alcohol [8]. These compounds have various applications in the industry, including pesticides and insecticides, plastics, engine lubricants and hydraulic fluids. Though very effective, OPs are incredibly toxic to life on earth, including humans. In this paper we will discuss the neurotoxicity of organic phosphates upon their release from car exhausts into the atmosphere, why they are added to lubricants, and their potential contribution to increasing incidence of cognitive issues in the general population.

| Background:

Organophosphates were first utilised in the 1930s as incredibly effective insecticides [5]. They can damage the enzyme acetylcholinesterase (AChE) [10], which plays a critical role in controlling nerve signals - the resulting damage kills pests.

OPs are most famously known as the "nerve gas" responsible for causing millions of deaths during Nazi Germany. Due to their ability to inhibit cholinesterase neurotransmitters, these toxins caused neuromuscular transmission dysfunction.

OPs such as Tabun, Sarin, Soman and VX kill in minutes. Making them effective mass neurotoxic weapons.

The OPs used in modern lubricants are not chemically identical to those used in neuro-gas. However, they exhibit very similar neurotransmitter inhibition properties and, though less severe, cause disruptions in cognitive function [12].

| ZDDP Additives:

Since the 1940s, OP additives have been integrated into engine oil and hydraulic fluids. The most popular lubricant additive today - ZDDP (zinc dialkyl-dithio-phosphate) - is an organophosphate-containing compound. Lubricants containing ZDDP represent a large proportion of total market by volume, thanks to ZDDP's excellent antiwear and antioxidant properties that can be achieved at low marginal cost.

New research criticises the large-scale use of ZDDP additives. ZDDP creates a reliable protective film over metal surfaces [4], composed of substances such as glassy iron and zinc polyphosphates. Though this technology has been successfully running the engine world for over 60 years, emissions concerns have cast doubt over its use in the future.

ZDDP additives are a hindrance to catalytic converters – where they poison the rare-earth catalysts that convert harmful 2 carbon monoxide into CO2. They are also the main source of many neurotoxic organophosphate compounds found in vehicle exhausts. The presence of OPs in our atmosphere is a potential concern to public health.

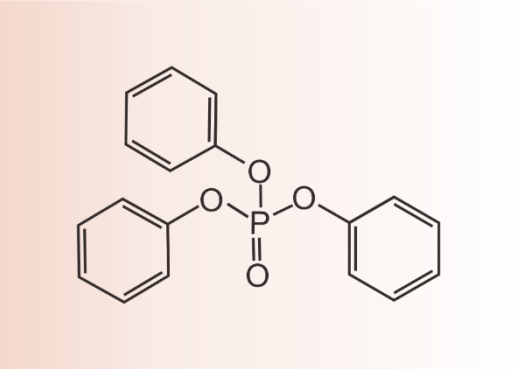
'Occurrence of organic phosphates in particulate matter of the vehicle exhausts and outdoor environment'

A case study [6] published by the scientific journal 'Environmental Pollution', on 16th October 2018, investigated OPs as potential emerging pollutants, particularly in pesticides, rural and industrial environments, and (most importantly) vehicle exhausts. The paper describing the investigation was written by

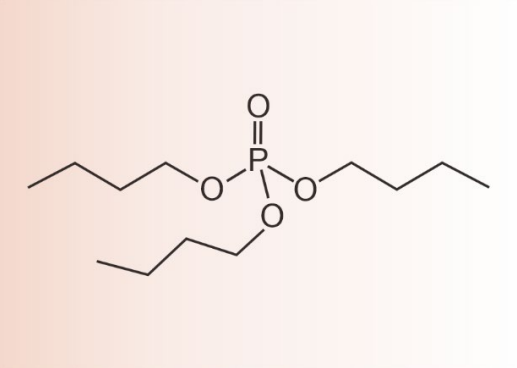
Monika J. Fabianska, Barbara Kozielska, Jan Konieczynski, and *Piotr Bielaczyc.*

Four major OPs found in vehicle exhausts included:

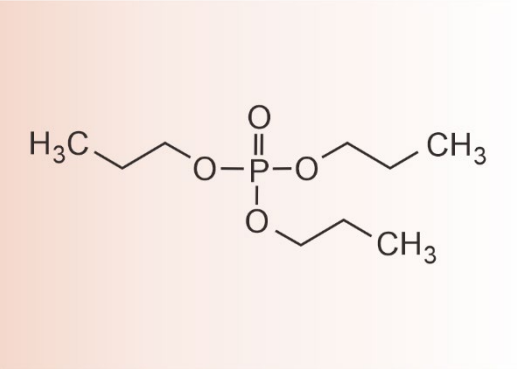
TPhP - Triphenyl phosphate; OP(OC6H5)3.



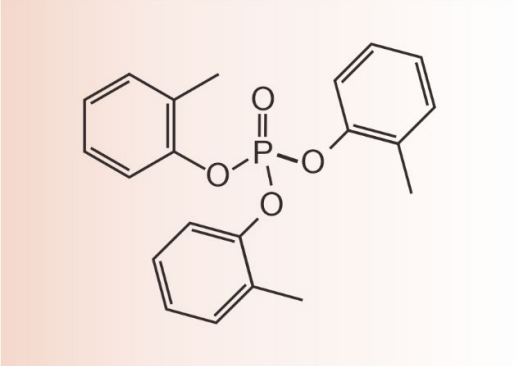
TBP - Tributyl phosphate; (COH9)3PO4.



TPP - Tripropyl phosphate; C9H21O4P.



TCP - Tricrecyl phosphate; C21H21O4P.



The study concluded that the concentration of OPs released was directly related to traffic levels.

"There is the exponential correlation between concentrations of two most common OPEs - TCiPP and TPhP (Fig. 2a). This indicates that both compounds, and other OPEs as well, are source related. The similar type of correlation exists between OPEs concentrations sums and concentrations sums of polycyclic aromatic hydrocarbons (PAHs) assessed previously for the same samples (Fabianska et al., 2016, 2017) (Fig. 2b). This shows that PAHs and OPEs both predominantly derive from the same source, i.e. dense traffic." [6]

Consider the widespread behaviours observed in the heavy traffic characteristics of densely populated cities. Countless individuals use the start-stop method when stuck in traffic jams [3]. This system is an effective fuel saving mechanism that reduces carbon emissions due to engines running for less time. The trade-off is an increase in organophosphate pollution.

"The UDC test begins with a cold start of the engine that requires the additional lubricant use. This also causes the additional emission of OPEs to the air since lubricants contain them." [6]

When an engine is started, the engine cylinder experiences an increase in both temperature and pressure. This creates the conditions to hydrolyse ZDDP into smaller organophosphates. Those chemicals then 3 leave the engine through exhaust pipes, along

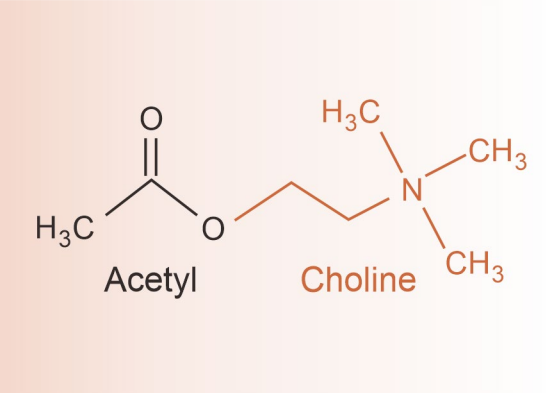
with other, more well-known pollutants such as COx and SOx.

| The Problem:

Humans exposed to OPs experience major negative side effects, including nausea, light-headedness, muscle tremors, confusion, etc. [7]. It is possible that their effect may be more significant than currently understood and have permanent effects on human mental health, stress levels, or even development.

Neurotic Dysfunction:

ACh is a neurotransmitter that plays a vital role in memory and stimulating muscle contractions. It is composed of two parts, Acetyl CoA, and Choline. The enzyme choline acetyltransferase facilitates the following reaction.



Sampled from [15]

There are two key enzymes in ACh chemistry - Choline Acetyl Transferase (ChAT) and Acetylcholinesterase (AChE). ChAT is responsible for ACh synthesis and helps bind its components - Acetyl CoA and Choline - to form ACh as a final product. AChE plays a slightly different role. This enzyme disassembles ACh into its base components after it has performed its function at a synapse Organophosphates inhibit the enzyme AChE from breaking down ACh, which causes ACh to accumulate in-between synapses [15][16]. They do so by altering the shape of the enzyme's active site. This prolongs the stimulation period of neurons and causes what is known as the Cholinergic Effect. The consequences of this include muscle contraction dysfunction, nausea and vomiting, reduced heart rate, bronchoconstriction, etc. If OP poisoning is not cleared within 24–48 hours, the AChE damage becomes irreversible [15][14].

OPs and Mental Distress:

Additionally, frequent acute exposure to organophosphate compounds has been identified as a contributor to the mental health crisis, particularly in big cities with heavy traffic.

"Recently, human imaging studies have revived the idea, first proposed in the 1970s, that increased cholinergic signalling can contribute to depression. Peripheral administration of the acetylcholinesterase (AChE) antagonist physostigmine induces symptoms of anxiety and depression in human subjects by decreasing the breakdown of ACh and increasing levels of the neurotransmitter in the brain" [source#] The inability for ACh to be broken down causes symptoms associated with anxiety and depression [10].

'Anxiety Associated with Exposure to OP Compounds'

This study [1], conducted by the Neuropsychological Laboratory, Department 4 of Neurology, University Hospitals, Iowa City, aimed to investigate the effect of frequent exposure to organophosphate compounds on mental health struggles such as anxiety and depression. The source of OPs came from pesticides, which farmers inhaled frequently due to rigorous work and potentially inadequate safety wear. Two groups of men were investigated - an exposure group and a control group. The exposure group consisted of 13 applicators and 11 farmers who had daily contact with pesticides during the spraying season, and the control group included 24

unaffected farmers, matched with the exposure group by age and education level.

Mental health and wellness levels were assessed in both groups in the form of psychiatric interviews during the trial. What the researchers found was that individuals in the exposure group had not only higher levels of anxiety but also higher concentrations of ChE in blood plasma. This showed a direct link between regular exposure to OPs and a decline in mental health.

Comparison of Control and Exposed Groups

Dependent Measure	Control (N = 24) $\bar{X}$	Control (N = 24) SD	Exposed (N = 24) $\bar{X}$	Exposed (N = 24) SD	Student *t* Test
Age, yr	38.83	9.96	39.17	5.93	.14
Education, yr	12.42	1.93	12.42	1.79	.00
Anxiety	9.88	6.35	14.46	8.49	2.12
Depression	3.29	3.82	3.92	3.19	.62
Symptom severity	1.79	2.59	2.92	4.65	1.04
Red blood cell cholinesterase	13.21	2.02	13.55	2.06	.01
Plasma cholinesterase	4.81	1.47	3.78	1.01	2.84

Sampled from [1]

The exposure group had a higher incidence of non-prescribed drug use (66% compared to 54% in CG), use of prescribed drugs to combat health issues (33% compared to 21% in CG), and consumption of high amounts of alcohol (29% compared to 13% in CG).

It is reasonable to conclude that the organophosphates inhaled from traffic have a similar or identical effect on our mental stability [9][13]. Given all OPs are known AChE inhibitors, it may be time so sound a note of \caution on regular exposure to car pollutants.

| Conclusion:

Increased stress levels and general mental health issues have been linked to organophosphate exposure. This issue should be addressed in the near term to avoid increasing rates of mental health distress. There has been a global mental health decline in the recent past; approximately 800,000 people commit suicide every year. Stress levels are higher than ever, and the numbers of children born with developmental disabilities increases day by day. Governments and environmental regulators should prioritize the removal of OPs as risk factors to mental health. By removing organophosphate additives from engine lubricants and hydraulic fluids, we can better our environment and save countless lives.

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