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POLLUTANTS AND THEIR IMPACT ON ENVIRONMENT

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ABSTRACT: Pollutants are toxic chemicals that adversely affect human health and the environment around the world. Because they can be transported by wind and water, most POPs generated in one country can and do affect people and wildlife far from where they are used and released.

The effect of POPs on human and environmental health was discussed, with intention to eliminate or severely restrict their production, by the international community at the Stockholm Convention on Persistent Organic Pollutants in 2001.

Most POPs are pesticides or insecticides, and some are also solvents, pharmaceuticals, and industrial chemicals.[1] Although some POPs arise naturally (e.g. from volcanoes), most are man-made.[2] The "dirty dozen" POPs identified by the Stockholm Convention include aldrin, chlordane, dieldrin, endrin, heptachlor, HCB, mirex, toxaphene, PCBs, DDT, dioxins, and polychlorinated dibenzofurans. However, there are many other PFOAs, for example PFASs.

KEYWORDS-persistent,organic,pollutants,environment,convention,impact,health

I. INTRODUCTION

Consequences of persistence

POPs typically are halogenated organic compounds (see lists below) and as such exhibit high lipid solubility. For this reason, they bioaccumulate in fatty tissues. Halogenated compounds also exhibit great stability reflecting the nonreactivity of C-Cl bonds toward hydrolysis and photolytic degradation. The stability and lipophilicity of organic compounds often correlates with their halogen content, thus polyhalogenated organic compounds are of particular concern. They exert their negative effects on the environment through two processes, long range transport, which allows them to travel far from their source, and bioaccumulation, which reconcentrates these chemical compounds to potentially dangerous levels.[3] Compounds that make up POPs are also classed as PBTs (persistent, bioaccumulative and toxic) or TOMPs (toxic organic micro pollutants).[4]

Long-range transport

POPs enter the gas phase under certain environmental temperatures and volatilize from soils, vegetation, and bodies of water into the atmosphere, resisting breakdown reactions in the air, to travel long distances before being re-deposited.[5] This results in accumulation of POPs in areas far from where they were used or emitted, specifically environments where POPs have never been introduced such as Antarctica, and the Arctic circle.[6] POPs can be present as vapors in the atmosphere or bound to the surface of solid particles (aerosols). A determining factor for the long-range transport is the fraction of a POP that is adsorbed on aerosols. In adsorbed form it is – as opposed to the gas phase – protected from photo-oxidation, i.e. direct photolysis as well as oxidation by OH radicals or ozone.[7][8]

POPs have low solubility in water but are easily captured by solid particles, and are soluble in organic fluids (oils, fats, and liquid fuels). POPs are not easily degraded in the environment due to their stability and low decomposition rates. Due to this capacity for long-range transport, POP environmental contamination is extensive, even in areas where POPs have never been used, and will remain in these environments years after restrictions implemented due to their resistance to degradation.[9][10]

Bioaccumulation

Bioaccumulation of POPs is typically associated with the compounds high lipid solubility and ability to accumulate in the fatty tissues of living organisms for long periods of time.[9][11] Persistent chemicals tend to have higher concentrations and are eliminated more slowly. Dietary accumulation or bioaccumulation is another hallmark characteristic of POPs, as POPs move up the food chain, they increase in concentration as they are processed and metabolized in certain tissues of organisms. [1,2,3]The natural capacity for animals gastrointestinal tract to concentrate

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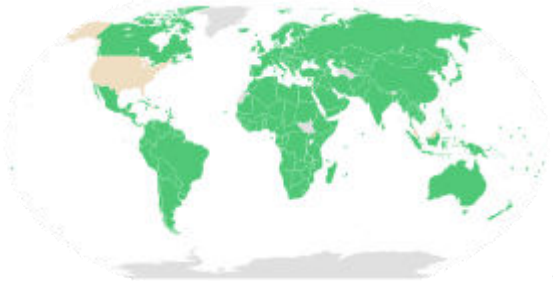
ingested chemicals, along with poorly metabolized and hydrophobic nature of POPs, makes such compounds highly susceptible to bioaccumulation.[12] Thus POPs not only persist in the environment, but also as they are taken in by animals they bioaccumulate, increasing their concentration and toxicity in the environment.[5][13] This increase in concentration is called biomagnification, which is where organisms higher up in the food chain have a greater accumulation of POPs.[14] Bioaccumulation and long-range transport are the reason why POPs can accumulate in organisms like whales, even in remote areas like Antarctica.[15]

Stockholm Convention on Persistent Organic Pollutants



State parties to the Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention was adopted and put into practice by the United Nations Environment Programme (UNEP) on May 22, 2001. The UNEP decided that POP regulation needed to be addressed globally for the future. The purpose statement of the agreement is "to protect human health and the environment from persistent organic pollutants." As of 2014, there are 179 countries in compliance with the Stockholm convention. The convention and its participants have recognized the potential human and environmental toxicity of POPs. They recognize that POPs have the potential for long range transport and bioaccumulation and biomagnification. The convention seeks to study and then judge whether or not a number of chemicals that have been developed with advances in technology and science can be categorized as POPs or not. The initial meeting in 2001 made a preliminary list, termed the "dirty dozen", of chemicals that are classified as POPs. As of 2021, the United States has signed the Stockholm Convention but has not ratified it. There are a handful of other countries that have not ratified the convention but most countries in the world have ratified the convention.[16]

Compounds on the Stockholm Convention list

In May 1995, the UNEP Governing Council investigated POPs.[17] Initially the Convention recognized only twelve POPs for their adverse effects on human health and the environment, placing a global ban on these particularly harmful and toxic compounds and requiring its parties to take measures to eliminate or reduce the release of POPs in the environment.[2][16][18]

1. Aldrin, an insecticide used in soils to kill termites, grasshoppers, Western corn rootworm, and others, is also known to kill birds, fish, and humans. Humans are primarily exposed to aldrin through dairy products and animal meats.
2. Chlordane, an insecticide used to control termites and on a range of agricultural crops, is known to be lethal in various species of birds, including mallard ducks, bobwhite quail, and pink shrimp; it is a chemical that remains in the soil with a reported half-life of one year. Chlordane has been postulated to affect the human immune system and is classified as a possible human carcinogen. Chlordane air pollution is believed the primary route of human exposure.[5,7,8]
3. Dieldrin, a pesticide used to control termites, textile pests, insect-borne diseases and insects living in agricultural soils. In soil and insects, aldrin can be oxidized, resulting in rapid conversion to dieldrin. Dieldrin's half-life is approximately five years. Dieldrin is highly toxic to fish and other aquatic animals, particularly frogs, whose embryos can develop spinal deformities after exposure to low levels. Dieldrin has been linked to Parkinson's disease, breast cancer, and classified as immunotoxic, neurotoxic, with endocrine disrupting capacity. Dieldrin residues have been found in air, water, soil, fish, birds, and mammals. Human exposure to dieldrin primarily derives from food.
4. Endrin, an insecticide sprayed on the leaves of crops, and used to control rodents. Animals can metabolize endrin, so fatty tissue accumulation is not an issue, however the chemical has a long half-life in soil for up to 12 years. Endrin is highly toxic to aquatic animals and humans as a neurotoxin. Human exposure results primarily through food.

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5. Heptachlor, a pesticide primarily used to kill soil insects and termites, along with cotton insects, grasshoppers, other crop pests, and malaria-carrying mosquitoes. Heptachlor, even at very low doses has been associated with the decline of several wild bird populations – Canada geese and American kestrels. In laboratory tests have shown high-dose heptachlor as lethal, with adverse behavioral changes and reduced reproductive success at low-doses, and is classified as a possible human carcinogen. Human exposure primarily results from food.
6. Hexachlorobenzene (HCB) was first introduced in 1945–59 to treat seeds because it can kill fungi on food crops. HCB-treated seed grain consumption is associated with photosensitive skin lesions, colic, debilitation, and a metabolic disorder called porphyria turcica, which can be lethal. Mothers who pass HCB to their infants through the placenta and breast milk had limited reproductive success including infant death. Human exposure is primarily from food.
7. Mirex, an insecticide used against ants and termites or as a flame retardant in plastics, rubber, and electrical goods. Mirex is one of the most stable and persistent pesticides, with a half-life of up to 10 years. Mirex is toxic to several plant, fish and crustacean species, with suggested carcinogenic capacity in humans. Humans are exposed primarily through animal meat, fish, and wild game.[9,10,11]
8. Toxaphene, an insecticide used on cotton, cereal, grain, fruits, nuts, and vegetables, as well as for tick and mite control in livestock. Widespread toxaphene use in the US and chemical persistence, with a half-life of up to 12 years in soil, results in residual toxaphene in the environment. Toxaphene is highly toxic to fish, inducing dramatic weight loss and reduced egg viability. Human exposure primarily results from food. While human toxicity to direct toxaphene exposure is low, the compound is classified as a possible human carcinogen.
9. Polychlorinated biphenyls (PCBs), used as heat exchange fluids, in electrical transformers, and capacitors, and as additives in paint, carbonless copy paper, and plastics. Persistence varies with degree of halogenation, an estimated half-life of 10 years. PCBs are toxic to fish at high doses, and associated with spawning failure at low doses. Human exposure occurs through food, and is associated with reproductive failure and immune suppression. Immediate effects of PCB exposure include pigmentation of nails and mucous membranes and swelling of the eyelids, along with fatigue, nausea, and vomiting. Effects are transgenerational, as the chemical can persist in a mother's body for up to 7 years, resulting in developmental delays and behavioral problems in her children. Food contamination has led to large scale PCB exposure.
10. Dichlorodiphenyltrichloroethane (DDT) is probably the most infamous POP. It was widely used as insecticide during WWII to protect against malaria and typhus. After the war, DDT was used as an agricultural insecticide. In 1962, the American biologist Rachel Carson published Silent Spring, describing the impact of DDT spraying on the US environment and human health. DDT's persistence in the soil for up to 10–15 years after application has resulted in widespread and persistent DDT residues throughout the world including the arctic, even though it has been banned or severely restricted in most of the world. DDT is toxic to many organisms including birds where it is detrimental to reproduction due to eggshell thinning. DDT can be detected in foods from all over the world and food-borne DDT remains the greatest source of human exposure. Short-term acute effects of DDT on humans are limited, however long-term exposure has been associated with chronic health effects including increased risk of cancer and diabetes, reduced reproductive success, and neurological disease.
11. Dioxins are unintentional by-products of high-temperature processes, such as incomplete combustion and pesticide production. Dioxins are typically emitted from the burning of hospital waste, municipal waste, and hazardous waste, along with automobile emissions, peat, coal, and wood. Dioxins have been associated with several adverse effects in humans, including immune and enzyme disorders, chloracne, and are classified as a possible human carcinogen. In laboratory studies of dioxin effects an increase in birth defects and stillbirths, and lethal exposure have been associated with the substances. Food, particularly from animals, is the principal source of human exposure to dioxins. Dioxins were present in Agent Orange, which was used by the United States in chemical warfare against Vietnam and caused devastating multi-generational effects in both Vietnamese and American civilians.[12,13,15]
12. Polychlorinated dibenzofurans are by-products of high-temperature processes, such as incomplete combustion after waste incineration or in automobiles, pesticide production, and polychlorinated biphenyl production. Structurally similar to dioxins, the two compounds share toxic effects. Furans persist in the environment and classified as possible human carcinogens. Human exposure to furans primarily results from food, particularly animal products.

II. DISCUSSION

New POPs on the Stockholm Convention list

Since 2001, this list has been expanded to include some polycyclic aromatic hydrocarbons (PAHs), brominated flame retardants, and other compounds. Additions to the initial 2001 Stockholm Convention list are the following POPs:[19][16]

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- Chlordecone, a synthetic chlorinated organic compound, is primarily used as an agricultural pesticide, related to DDT and Mirex. Chlordecone is toxic to aquatic organisms, and classified as a possible human carcinogen. Many countries have banned chlordecone sale and use, or intend to phase out stockpiles and wastes.
- α-Hexachlorocyclohexane (α-HCH) and β-Hexachlorocyclohexane (β-HCH) are insecticides as well as by-products in the production of lindane. Large stockpiles of HCH isomers exist in the environment. α-HCH and β-HCH are highly persistent in the water of colder regions. α-HCH and β-HCH has been linked Parkinson's and Alzheimer's disease.
- Hexabromodiphenyl ether (hexaBDE) and heptabromodiphenyl ether (heptaBDE) are main components of commercial octabromodiphenyl ether (octaBDE). Commercial octaBDE is highly persistent in the environment, whose only degradation pathway is through debromination and the production of bromodiphenyl ethers, which can increase toxicity.
- Lindane (γ-hexachlorocyclohexane), a pesticide used as a broad spectrum insecticide for seed, soil, leaf, tree and wood treatment, and against ectoparasites in animals and humans (head lice and scabies). Lindane rapidly bioconcentrates. It is immunotoxic, neurotoxic, carcinogenic, linked to liver and kidney damage as well as adverse reproductive and developmental effects in laboratory animals and aquatic organisms. Production of lindane unintentionally produces two other POPs α-HCH and β-HCH.[
- Pentachlorobenzene (PeCB), is a pesticide and unintentional byproduct. PeCB has also been used in PCB products, dyestuff carriers, as a fungicide, a flame retardant, and a chemical intermediate. PeCB is moderately toxic to humans, while highly toxic to aquatic organisms.[17,18,19]
- Tetrabromodiphenyl ether (tetraBDE) and pentabromodiphenyl ether (pentaBDE) are industrial chemicals and the main components of commercial pentabromodiphenyl ether (pentaBDE). PentaBDE has been detected in humans in all regions of the world.
- Perfluorooctanesulfonic acid (PFOS) and its salts are used in the production of fluoropolymers. PFOS and related compounds are extremely persistent, bioaccumulating and biomagnifying. The negative effects of trace levels of PFOS have not been established.
- Endosulfans are insecticides to control pests on crops such coffee, cotton, rice and sorghum and soybeans, tsetse flies, ectoparasites of cattle. They are used as a wood preservative. Global use and manufacturing of endosulfan has been banned under the Stockholm convention in 2011, although many countries had previously banned or introduced phase-outs of the chemical when the ban was announced. Toxic to humans and aquatic and terrestrial organisms, linked to congenital physical disorders, mental retardation, and death. Endosulfans' negative health effects are primarily liked to its endocrine disrupting capacity acting as an antiandrogen.
- Hexabromocyclododecane (HBCD) is a brominated flame retardant primarily used in thermal insulation in the building industry. HBCD is persistent, toxic and ecotoxic, with bioaccumulative and long-range transport properties.

Health effects

POP exposure may cause developmental defects, chronic illnesses, and death. Some are carcinogens per IARC, possibly including breast cancer.[1] Many POPs are capable of endocrine disruption within the reproductive system, the central nervous system, or the immune system. People and animals are exposed to POPs mostly through their diet, occupationally, or while growing in the womb.[1] For humans not exposed to POPs through accidental or occupational means, over 90% of exposure comes from animal product foods due to bioaccumulation in fat tissues and bioaccumulate through the food chain. In general, POP serum levels increase with age and tend to be higher in females than males.[11]

Studies have investigated the correlation between low level exposure of POPs and various diseases. In order to assess disease risk due to POPs in a particular location, government agencies may produce a human health risk assessment which takes into account the pollutants' bioavailability and their dose-response relationships.[20]

Endocrine disruption

The majority of POPs are known to disrupt normal functioning of the endocrine system. Low level exposure to POPs during critical developmental periods of fetus, newborn and child can have a lasting effect throughout their lifespan. A 2002 study[21] summarizes data on endocrine disruption and health complications from exposure to POPs during critical developmental stages in an organism's lifespan. The study aimed to answer the question whether or not chronic, low level exposure to POPs can have a health impact on the endocrine system and development of organisms from different species. The study found that exposure of POPs during a critical developmental time frame can produce a permanent changes in the organisms path of development. Exposure of POPs during non-critical developmental time frames may

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not lead to detectable diseases and health complications later in their life. In wildlife, the critical development time frames are in utero, in ovo, and during reproductive periods. In humans, the critical development timeframe is during fetal development.[21]

Reproductive system

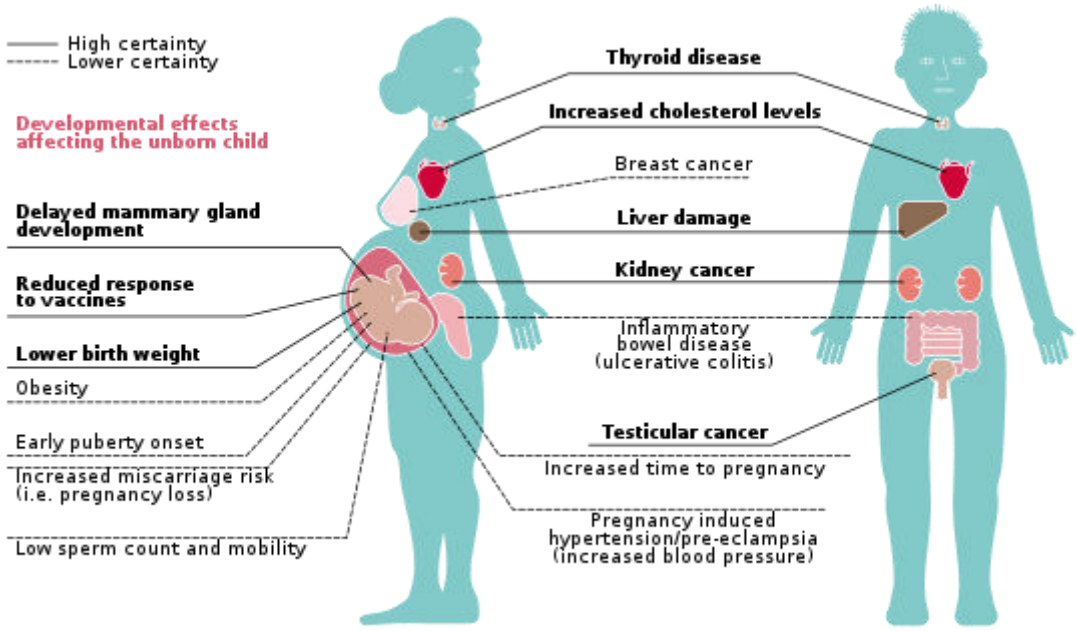
The same study in 2002[21] with evidence of a link from POPs to endocrine disruption also linked low dose exposure of POPs to reproductive health effects. The study stated that POP exposure can lead to negative health effects especially in the male reproductive system, such as decreased sperm quality and quantity, altered sex ratio and early puberty onset. For females exposed to POPs, altered reproductive tissues and pregnancy outcomes as well as endometriosis have been reported.[2]

Gestational weight gain and newborn head circumference[20,21,22]

A Greek study from 2014 investigated the link between maternal weight gain during pregnancy, their PCB-exposure level and PCB level in their newborn infants, their birth weight, gestational age, and head circumference. The lower the birth weight and head circumference of the infants was, the higher POP levels during prenatal development had been, but only if mothers had either excessive or inadequate weight gain during pregnancy. No correlation between POP exposure and gestational age was found.[22] A 2013 case-control study conducted 2009 in Indian mothers and their offspring showed prenatal exposure of two types of organochlorine pesticides (HCH, DDT and DDE) impaired the growth of the fetus, reduced the birth weight, length, head circumference and chest circumference.[23][24]

III. RESULTS

Health effects of PFAS



Effects of exposure to PFASs on human health[25][26][27][28][29][30]

Hormone-disrupting chemicals, including PFASs, are linked with rapid declines in human fertility.[31] In a meta-analysis for associations between PFASs and human clinical biomarkers for liver injury, authors considered both PFAS effects on liver biomarkers and histological data from rodent experimental studies and concluded that evidence exists showing that PFOA, perfluorohexanesulfonic acid (PFHxS), and perfluorononanoic acid (PFNA) are hepatotoxic to humans.[32]

Many comprehensive epidemiological studies linking adverse human health effects to PFASs, particularly PFOA, come from the C8 Science Panel.[33] The panel was formed as part of a contingency to a class action lawsuit brought by communities in the Ohio River Valley against DuPont in response to landfill and wastewater dumping of PFAS-laden material from DuPont's West Virginia Washington Works Plant.[33] The panel measured PFOA (also known as C8) serum concentrations in 69,000 individuals from around DuPont's Washington Works Plant and found a mean concentration of 83.0 ng/mL, compared to 4 ng/mL in a standard population of Americans.[34] This panel reported

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probable links between elevated PFOA blood concentration and hypercholesterolemia, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer as well as pregnancy-induced hypertension and preeclampsia.

Additive and synergistic effects

Evaluation of the effects of POPs on health is very challenging in the laboratory setting. For example, for organisms exposed to a mixture of POPs, the effects are assumed to be additive.[40] Mixtures of POPs can in principle produce synergistic effects. With synergistic effects, the toxicity of each compound is enhanced (or depressed) by the presence of other compounds in the mixture. When put together, the effects can far exceed the approximated additive effects of the POP compound mixture.[3]

In urban areas and indoor environments

Traditionally it was thought that human exposure to POPs occurred primarily through food, however indoor pollution patterns that characterize certain POPs have challenged this notion. [23,25,27]Recent studies of indoor dust and air have implicated indoor environments as a major sources for human exposure via inhalation and ingestion.[41] Furthermore, significant indoor POP pollution must be a major route of human POP exposure, considering the modern trend in spending larger proportions of life indoors. Several studies have shown that indoor (air and dust) POP levels to exceed outdoor (air and soil) POP concentrations.[40]

In rainwater

In 2021, it was found that levels of at least four perfluoroalkyl acids (PFAAs) in rainwater worldwide ubiquitously and often greatly exceeded the EPA's lifetime drinking water health advisories as well as comparable Danish, Dutch, and European Union safety standards, leading to the conclusion that "the global spread of these four PFAAs in the atmosphere has led to the planetary boundary for chemical pollution being exceeded".[42] There are some moves to restrict and replace their use.[43]

In cosmetics and personal care products

Per- and polyfluoroalkyl substances (PFAS) are a class of about 9,000 synthetic organofluorine compounds that have multiple highly toxic fluorine atoms attached to an alkyl chain. PFAS are used in the manufacture of a wide range of products such as food packaging and clothing. They are also used by major companies of the cosmetics industry in a wide range of cosmetics, including lipstick, eye liner, mascara, foundation, concealer, lip balm, blush, nail polish and other such products. A 2021 study tested 231 makeup and personal care products and found organic fluorine, an indicator of PFAS, in more than half of the samples. High levels of fluorine were most commonly identified in waterproof mascara (82% of brands tested), foundations (63%), and liquid lipstick (62%). Since PFAS compounds are highly mobile, they are readily absorbed through human skin and through tear ducts, and such products on lips are often unwittingly ingested. Manufacturers often fail to label their products as containing PFAS, which makes it difficult for cosmetics consumers to avoid products containing PFAS.[44]

Control and removal in the environment

Current studies aimed at minimizing POPs in the environment are investigating their behavior in photocatalytic oxidation reactions. POPs that are found in humans and in aquatic environments the most are the main subjects of these experiments. Aromatic and aliphatic degradation products have been identified in these reactions. Photochemical degradation is negligible compared to photocatalytic degradation.[2] A method of removal of POPs from marine environments that has been explored is adsorption. It occurs when an absorbable solute comes into contact with a solid with a porous surface structure. This technique was investigated by Mohamed Nageeb Rashed of Aswan University, Egypt.[45] Current efforts are more focused on banning the use and production of POPs worldwide rather than removal of POPs.[11]

IV. CONCLUSIONS

The term environmental persistent pharmaceutical pollutants (EPPP) was first suggested in the nomination in 2010 of pharmaceuticals and environment as an emerging issue in a Strategic Approach to International Chemicals Management (SAICM)[1] by the International Society of Doctors for the Environment (ISDE). The occurring problems from EPPPs are in parallel explained under environmental impact of pharmaceuticals and personal care products (PPCP). The European Union summarizes pharmaceutical residues with the potential of contamination of water and soil together with other micropollutants under "priority substances".[2]

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Background

Pharmaceuticals comprise one of the few groups of chemicals that are specifically designed to act on living cells, which presents a special risk when they enter, persist and are dispersed into the environment.

With the exception of watercourses downstream of sewage treatment plants, the concentration of pharmaceuticals in surface and ground water is generally low. Concentrations in sewage sludge and in landfill leachate may be substantially higher[3] and provide alternative routes for EPPPs to enter the human and animal food-chain.

However, even at very low environmental concentrations, the chronic exposure to environmental pharmaceuticals chemicals can add to the effects of other chemicals in the cocktail is still not studied. The different chemicals might be potentiating synergistic effects (higher than additive effects). An extremely sensitive group in this respect are foetuses.

EPPPs are already found in water all over the world. The diffuse exposure might contribute to

- extinction of species and imbalance of sensible ecosystems, as many EPPPs affect the reproductive systems of for example frogs, fish and mussels;[
- genetic, developmental, immune and hormonal health effects to humans and other species, in the same way as e.g. oestrogen-like chemicals;[
- development of microbes resistant to antibiotics, as is found in India.[4]

Environmental classification of pharmaceuticals

In Sweden, the industry together with universities and health care sector has developed a method for environmental risk assessment and environmental classification of drugs.[5][6] Environmental risk refers to the risk of toxicity to the aquatic environment. It is based on the ratio between predicted environmental concentration of the substance (PEC) and the highest concentration of the substance that does not have a harmful effect in the environment (PNEC).

Environmental hazard expresses the inherent environmentally damaging characteristics of the substance in terms of persistence, bioaccumulation and toxicity. The toxicity tests used are acute toxicity of fish, acute toxicity of Daphnia sp. and growth inhibition test of algae. Most medications on the Swedish market are now classified. This gives the health care possibilities to make better choices when prescribing medicines.

Exposure

Concentrations in surface waters, groundwater and partially treated water are typically less than 0.1 µg/L (or 100 ng/L), and concentrations in treated water are generally below 0.05 µg/L (or 50 ng/L).(ny 8 WHO)[However, all water on the earth is part of the same stable pool, and as larger amounts of pharmaceuticals are consumed, there is a risk that the concentration of pharmaceuticals in drinking water will increase

Release into the environment

Pharmaceuticals reach the environment and cause water pollution mainly in three ways:

- They are excreted from humans and animals, intact or metabolised, mainly into the urine, passing on to the environment directly or via sewage treatment plants.
- Unused pharmaceuticals reach the environment either via household wastewater or via urban solid garbage handling.
- Manufacturing plants producing the active substances might unintentionally release pharmaceuticals into the environment.[28,29]

Due to improved measurement methods pharmaceuticals may be detected today in concentrations that probably have been present already for decades but could not be measured before. Many pharmaceuticals are (after consumption) excreted or washed off: investigations have shown excretion rates between 30% and 70% of orally taken substances[7] and even higher rates considering externally applied ointments or gel.[8]

Some pharmaceuticals are degraded to various extents in sewage treatment plants, but others leave the plant in active forms. Active residues of pharmaceuticals have been detected in surface water, and they may persist in the environment for long periods of time.[Large amounts of antibiotics and other pharmaceuticals have been found downstream from sewage treatment plants in sub catchments where the discharge of hospital waste water plays a major role [9] or in catchments with pharmaceutical industries. EPPPs from treated sewage sludge used as fertilizer are absorbed by soya, and antibiotics have been found in the leaves.

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Drinking water

There are various pathways how pharmaceutical substances may enter drinking water. Predominantly, drinking water procurement comes from drinking water reservoirs, groundwater and bank filtration. If treated waste water is discharged in catchments with drinking water procurement the not eliminated pharmaceutical substances may be detected in the drinking water. The Netherlands for example gain 37% of their drinking water from surface water, mainly from bank filtration at Rhine and Meuse. Here certain attention is paid to pharmaceutical residues.[10]

In Germany drinking water catchments and rivers EPPPs have been detected already, especially radiocontrast agents.[11] Moreover, pharmaceutical residues here partly have their origin in agriculture.[12] An evaluation of the German Federal Environment Agency of regional investigations carried out between 2009 and 2011 showed in total 27 different pharmaceutical substances in concentrations of more than 0.1 microgram per litre in German surface waters and up to 150 substances have been detected in total. Besides the radiocontrast agents especially the painkiller diclofenac showed relevant concentrations.[13] For many micropollutants such as pharmaceuticals no threshold values in drinking water purification or waste water treatment are obligatory by now as the knowledge about effects is lacking or insufficiently proven.[14]

Some of these environmental pharmaceuticals chemicals are well known to have serious genotoxic effects in humans.[- life in nature varies depending on the environment (air, water, soil, sludge), but is more than one year for several compounds.[15][16][17]

Concentrations of EPPPs can vary from 1 ng to 1 mg per litre (2). Serious effects of EPPPs on water-living organisms, especially on reproductive systems, have been already shown, as well as on microbial communities.[17][18][19][20][

This would be of much less concern if the population were to keep their excrement out of the wastewater via the use of the urine-diverting dry toilet or systems that recycle treated blackwater to flush toilets again indefinitely.

Assessment

- Pharmaceuticals are special kinds of chemicals. They are manufactured to be biologically active in living organisms.
- The levels of pharmaceuticals in surface or drinking water are generally below 1 mg per litre, often measured in ng per litre (2, 8). This low concentration might appear to guarantee that they hardly pose any problem to public health. Assuming a concentration of 100 ng/L of a pharmaceutical that in humans has DDD (defined daily dose) of 10 mg implies that a volume of 100,000 litres would be required to make up one single DDD. Such calculation does not take into account the vulnerable population exposure for example during the period of development.
- Therapeutic levels of levonorgestrel (a sex hormone) has been found in rainbow trout downstream a sewage treatment plant.[21]

Laws and regulations

Environmental persistent pharmaceutical pollutants (EPPP) have to be looked at in their entirety of the product chain.[22] Pharmaceutical residues may enter the environment in various phases and therefore the influence or impact regarding environmental effects can be regulated on different levels:[9]

- on the scientific and industrial level of development and production,
- on the governmental and administrative level of authorization, market regulation and legislation,
- on the level of health insurances and their influence on production and consumption,
- on the distribution level with physicians and their prescriptions respectively in pharmacies and stores,
- on the level of patients with individual consumption pattern, disposal behavior etc. and finally
- in the field of waste management, waste water treatment and drinking water supply.

Pharmaceuticals differ from other anthropogenic chemicals with respect to legal requirements and depending on the countries and cultural frame. Partly they are excluded in laws and regulations which control manufacture, marketing, use, and disposal of other consumer products of a chemical character (solvents, paints, glues etc.). As a consequence the possible negative environmental impact of pharmaceuticals may be less documented, in comparison to other consumer chemicals.

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Laws and regulations in the European Union

In the European Union (EU) today more than 3,000 pharmaceutical substances are approved.[23] In 2013 the EU started initiatives to address to the task of pharmaceutical residues in the water cycle. Here the commission was proposing to add 15 chemicals to the watch list of substances in the Water Framework Directive (WFD)[24] that are monitored and controlled in EU surface waters, including 3 pharmaceuticals (besides industrial chemicals, substances used in biocides and plant protection products): "The contamination of water and soil with pharmaceutical residues is an emerging environmental concern. In evaluating and controlling the risk to, or via, the aquatic environment from medicinal products, adequate attention should be paid to Union environmental objectives. In order to address that concern, the Commission should study the risks of environmental effects from medicinal products and provide an analysis of the relevance and effectiveness of the current legislative framework in protecting the aquatic environment and human health via the aquatic environment."[2]

The two hormones estradiol and ethinylestradiol and the painkiller diclofenac are present on the list since 2013 and in 2015 three macrolide antibiotics were added, too.[25] In 2018, due to "sufficient high-quality monitoring data are available for the substances tri-allate, oxadiazon, 2,6-ditert-butyl-4-methylphenol and diclofenac, those substances should be removed from the watch list" and that "new ecotoxicological information for the macrolide antibiotics clarithromycin and azithromycin, for methiocarb, and for the neonicotinoids imidacloprid, thiacloprid and thiamethoxam, which led it to revise the predicted no-effect concentrations for those substances". The objective of the implementation of the WFD watch list is to update the available information on the fate of the listed substances in the aquatic environment and consequently, to support a more detailed environmental risk assessment. A preparatory"study on the environmental risks of medicinal products" was commissioned by the Executive Agency for Health and Consumers and published in December 2013. This "BIO IS study" discusses a wide range of legislative and non-legislative "factors of influence" and related possible solutions.[8]

According to the 2013 Directive "the Commission shall [...until September 2015] develop a strategic approach to pollution of water by pharmaceutical substances. That strategic approach shall, where appropriate, include proposals enabling, to the extent necessary, the environmental impacts of medicines to be taken into account more effectively in the procedure for placing medicinal products on the market. In the framework of that strategic approach, the Commission shall, where appropriate, by 14 September 2017 propose measures to be taken at Union and / or Member State level, as appropriate, to address the possible environmental impacts of pharmaceutical substances [...] with a view to reducing discharges, emissions and losses of such substances into the aquatic environment, taking into account public health needs and the cost effectiveness of the measures proposed."[2]

Beyond the precautionary approach the EU was already aiming at proper disposal practices since 2004. An EU directive for human pharmaceuticals explicitly requires that all member states should establish collection systems for unused or expired medicines. Such systems were already in use in several member states at the time the legislation went into action in 2004.[26] The disposal regulations in the EU member states are still rather different, ranging from recommendations to throw unused or expired pharmaceuticals into the household waste that goes nearly completely to incineration (Germany)[27] with temperatures usually between 900–1,300 °C[28] to collection systems where leftovers are considered to be "hazardous waste" (Luxembourg).[29]

In France, the Cyclamed take-back program[30] enables people to bring back unused or expired pharmaceuticals back to the pharmacies. Wrong disposal via sink or toilet and hereby to the wastewater system still seems to be a problem in many EU member states: investigations in Germany showed that up to 24% of liquid pharmaceuticals and 7% of tablets or ointments are disposed always or at least "rarely" via the toilet or sink.[9]

This is one of the aspects considered in the above-mentioned EU strategic approaches. Moreover, regarding the market authorization for pharmaceuticals approved for marketing in the EU before 2006 the environmental assessment criteria have been different. In case the active substance of a human medicinal product today is assessed to be a hazardous substance or assessed to pose a risk to the environment: no refusal of the product is possible, even though in 2012 about 1,200 pharmaceutical substances were identified to be potentially relevant for an environmental monitoring.[31]

Effects of pharmaceuticals in the environment

Estradiol (estrogen, synthetic hormone)

Concentrations in surface water alone are not sufficient to assess the risk of negative environmental effects in the aquatic environment. Synthetic hormones are endocrine disruptors. Thus, estrogenic compounds like ethinylestradiol (estrogen hormone) at concentrations < 1 ng per litre may cause both vitellogenin production (a frequently used index for feminization of male fish), and structural change in their sex organs. It has also been demonstrated that fish exposed to sewage treatment plant (STP) effluent can take up and concentrate estrogenic compounds, including ethinylestradiol,

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to very high internal levels. These observations on feminization of fish by estrogenic compounds in STP effluents have been observed in many countries, and have also been observed in other species, like frogs, alligators and molluscs.

Cardiovascular medicines

Other examples of environmental impact in the aquatic environment of human medication concern both cardiovascular and neuro-psychiatric medicines. The non-selective beta-blocking agent propanolol was found to cause a significant decrease in egg production in medaka fish, at a concentration close to that demonstrated in the sewage treatment plants (STP) effluents.[Gemfibrozil (cholesterol and triglycerides lowering drug) often appears in the effluent from STPs. At concentrations close to those reported in STP effluent, gemfibrozil lowers the blood levels of testosterone in fish.[

Citalopram / Fluoxetine (serotonin reuptake inhibitor anti depressants, SSRIs)

Some SSRIs have been shown to accumulate in exposed fish.[32][Citalopram has been detected in liver from wild perch in low µg per kg levels, and fluoxetine affects the serotonin system in the same way that it does in humans. Fluoxetine has also been shown to affect swimming activity in shellfish; whether this is linked to a disturbance of serotonin function in the brain is still unknown.

Antibiotics

High levels of antibiotics in the water are a cause for alarm as there is an increased risk of selecting resistant bacteria, an issue of global concern. This can lead to some highly effective antibiotics becoming ineffective. There are several examples: In India, bacteria resistant to ciprofloxacin have been found downstream pharmaceutical plants, genes for multi resistance were found in drinking water, and multi resistant Salmonella in water sprayed on vegetables. From Europe we know about the epidemic with multi resistant EHEC in summer 2011, originating from water sprayed vegetables.

The term "eco-shadow" has been introduced to describe the ecological impact of antibiotics. Antibiotics with a wide spectrum that are also stable will have a greater impact on the bacterial flora (a long eco-shadow) than those with a narrow antibacterial spectrum which disintegrates more rapidly (a short eco-shadow).

The ecological effects of tetracyclines and quinolones have been observed. They are not metabolized in the human body and are therefore excreted unmodified. When entered into the environment they are poorly degraded. They can be toxic to other animals, affecting particularly microorganism and fish. In the effluent from a sewage treatment plant in India, several broad spectrum antibiotics were found in concentrations toxic to bacteria and plants. In the sewage treatment plant itself, there were enterococcae resistant to all known antibiotics.

The development of resistant bacteria in sewage treatment plants is stimulated by high concentration of antibiotics (e.g. in plant sewage), large amounts of bacteria (e.g. from human sewage water that is added in plant sewage), and selection of Information that can be used to assess the nominated issue have been observed.

Gaps in knowledge

Effective environmental detection methods have to be developed and global detection strategy applied to map the current global situation.[

There are currently no test methods to assess whether negative effects may occur after long-term environmental diffuse exposure in humans, during the vulnerable periods of development, on aquatic micro-organism or how it may affect other animals.[Therefore, the precautionary principle must be guiding.

Concentrations in surface water alone are not sufficient to assess the risk of negative environmental effects of these synthetic chemicals. Consideration must be taken to bio-accumulation in fish and other aquatic food used by humans, as well as to additive and synergetic effects between pharmaceutical and other chemicals in the contaminated water.[

In a small study, several pharmaceuticals were found in milk of goat, cow and human.[33] More research is needed to find out how common this is, the concentrations and the sources[30]

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