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Open Chem., 2015; 13: 1353–1370

Chromatography **Open Access**

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Research trends on emerging environment pollutants – a review

DOI: 10.1515/chem-2015-0151
received January 6, 2015; accepted November 9, 2015.

Abstract: Concern for the natural environment increasingly devotes more attention to growing potential hazards resulting from the release of various substances. Currently, one of the main problems associated with environmental pollution is the derivation of organic compounds from wastewater. Substances derived from sewage leaks into the environment in the form of a multicomponent mixtures often enhances the toxic effects caused by these compounds. While analyzing the reports in the literature of the last two decades it can be seen that substantial efforts are devoted to the determination of selected trace contaminants present in wastewater. Among the most marked there are endocrine disrupting compounds, residues of pharmaceuticals and personal care products, plastics and sunscreens. Recently, a new group of compounds joined the aforementioned contaminants, namely drugs, whose legality and availability is increasing every year. Exposure to these type of compounds, named in the literature as emerging contaminants (ECs), involves, among others, such effects as hormonal imbalance, reduction of the survivability of aquatic organisms and reproductive problems.

This paper provides a review of the types of emerging organic groundwater contaminants (EGCs) which are beginning to be found in the natural environment in many countries all around the world.

Keywords: Emerging contaminants, endocrine disrupting compounds, environmental pollution, drugs, sunscreens

1 Introduction

Due to concern about the state of the natural environment, more and more attention is being given to the growing potential risks resulting from the release of various substances to the environment as a result of human activity. Main sources of anthropogenic pollution are the following: polluted wastewater, leachate from landfills and dumps, fertilizers and pesticides, petroleum substances released as a result of failure of pipelines, tankers and others. The compounds that are of particular interest for environmental monitoring specialists are those which are detected in significant quantities and have a high biological activity.

Organic compounds previously not known to be significant in freshwater, in terms of distribution and/or concentration, are now being more widely detected as analytical techniques improve [1]. These compounds, which have the potential to cause known or suspected adverse ecological or human health effects, are often collectively referred to as emerging contaminants (ECs) [2]. ECs include newly synthesized substances as well as ones that have long been present in the environment but whose presence and significance are only now being elucidated [3]. They include a wide array of different compounds and their transformation products: pharmaceuticals, personal care products, pesticides, veterinary products, industrial compounds/by-products, food additives, and engineered nano-materials [4-10]. An estimated 23 million chemicals have been indexed, with more than 7 million commercially available but only 230,000 are inventoried or regulated by governments worldwide [11].

A large range of toxic chemicals, re-released in everyday life, may in fact be a source of danger for the proper functioning of living organisms. Particular attention should be paid to the aquatic environment – both natural and artificial water reservoirs. Detection and determination of active forms of organic compounds in aquatic ecosystems is one of the priority tasks of environmental chemistry. A key problem for assessing the organic contamination in the water samples is the fact that a large group of hazardous compounds is

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present in trace amounts, often almost impossible to determine. This problem over the years was a challenge for analytical chemists, who are trying to develop more appropriate procedures intended for the determination of trace amounts of a wide variety of organic compounds in water samples with complex matrices. Striving to meet the principles of green chemistry analysis, which stem directly from the premises of sustainable development, it is the driving force of research and development of new analytical procedures and the construction of measuring devices.

Among all the emerging contaminants, endocrine disrupting compounds, residues of pharmaceuticals, and personal care product remains are widely observed as the most dangerous ones, these are briefly discussed below.

2 Endocrine disrupting compounds

Endocrine disrupting compounds (EDCs) compose a large group of compounds potentially interfering with natural biological functions by blocking the hormones, imitation, change or even destruction of their natural activity in living organisms. These compounds may include substances from the group of pesticides, softeners (plasticizers) such as organochlorides pesticides (OCP), organophosphate pesticides (OPP), phthalates, polychlorinated biphenyls (PCBs), polybrominateddiphenylethers (PBDE), brominated flame retardants (BFR), perfluorocarbons (PFC), antibiotics, non-steroidal anti-inflammatory agents, cardiovascular drugs, hormonal agents and surface active compounds and their metabolites (phenols). Most of them are ubiquitous and extremely persistent in the environment, bio-accumulate in the food chain, and can be stored in adipose tissue, where it is slowly metabolized and excreted [2].

In the main part, EDCs are of natural origin. However, more and more compounds belonging to this group are synthetic substances, produced and introduced to the natural environment in different ways. Such compounds are called xenoestrogens (environmental estrogens).

Xenoestrogens show the ability to interact with the endocrine system, disrupting its normal operation. They are mainly related with estrogen-based drugs, such as contraceptives, and hormones used in hormone-replacement therapy. It was observed that these substances cause side effects such as impaired fertility, lack of masculine features, etc. This phenomena is particularly observed for marine environment and water-related wildlife. Also for humans – xenoestrogens are present in drinking water, causing fertility problems in men and gender disorders in shaping human fetal life. These compounds are also detectable in plastic bottles, toys for children, in cosmetics, food packaging, in natural waters polluted urban wastewater, in water from swimming pools, and finally in processed foods (meat, soy products).

Published results of the medical and environmental research indicate that EDCs may cause hormonal disturbances, both temporal and permanent, especially prevalent for fetuses , due to their small size, high dynamics of growth processes, and reduced ability to detoxify harmful substances [12]. It was observed that several EDCs are able to pass through the placenta to the fetus. Many recent studies were devoted to the transmittance of EDC and assessing their content in the cord blood serum and maternal adipose tissue [13-26], showing that a fetus and once born an infant may be exposed to significantly high levels of EDC [27]. This can result in a decrease in fetal birth weight, premature birth, psychomotor retardation and altered cognitive function [28-33].

The literature review shows how EDC, gathered in the mother's body, is released from the mother's blood via the placenta, affecting the development of the fetus. In the past few years a correlation has been found between sudden infant death syndrome (SIDS) and sudden unexpected death syndrome intrauterine (SIUDS) with exposure to EDC indicating growing serious problems in this matter [34-37]. Both of these syndromes are among the most important causes of death in fetuses and neonates in developed countries. Still unknown are the reasons for their occurrence. Results focusing on defining the content of EDC in the tissues of fetuses and newborns has recently appeared in the literature.

The aim of this study was to develop a rapid and sensitive method for assessing the presence of EDC in tissues from fetuses and newborns who died from SIUDS or SIDS. Analyses were performed on samples from dead fetuses before the 25th week of pregnancy and from newborns who died under mysterious circumstances, diagnosed with SIDS. The victims came from areas of northern Italy, where intensive agricultural cultivation is carried out. Given the conditions in the environment from which the samples were collected, there were selected twenty five active endocrine compounds. These were derived from the group of EDC, including organochloride pesticides (OCP), organophosphate pesticides (OPP), and N-substituted carbamionic acids. Choosing OCP derivatives was associated with the widespread occurrence of this type of pollution in rural areas, and the well-known effects of exposure to the OCP. These compounds are also known to be the cause of miscarriages and delayed brain development [38]. On the other hand, OPP and carbamates are widely used in Italian agriculture as effective pesticides [39]. The study found an interesting correlation between the presence of these compounds herein, and the incidence of SIUDS and SIDS. However, it is difficult at this point to formulate clear conclusions, because these pioneering studies are based on too small a sample.

As for the presence, the sources, and the impact of estrogens on the natural environment, this is a complex problem for eco-toxicologists. Some of the researches consider, as the main source of endocrine active compounds, oral contraceptives widely used by women around the world e.g. in the United States alone contraceptives or hormone replacement therapy is used nearly 12 million women. Research conducted by A. Wise and colleagues, however, questioned these conclusions [40]. The authors argue that a certain amount of estrogen comes from the urine of all people: women, men, children, with most related to pregnant women. According to the researchers, as much as 90% of the polluting estrogen comes from the breeding animal manure. These results do not change the fact that long-term exposure to even low concentrations of active endocrine compounds may adversely affect human health [41]. Increased presence of the hermaphrodite fish populations in the reservoirs fed with purified water flowing from sewage treatment plants was observed in the US, Asia and Europe [42-44]. Still, however, there is a need to prove a direct relation between the presence of estrogens in surface waters, and changes in the sexuality of fish populations found in rivers, lakes and streams. In the literature, one can also find outstanding reports about the effects of hormone present in the aquatic environment on the growth of human reproductive problems [45].

3 Bisphenol-A

Recently, the presence of bisphenol-A (BPA) (4'-dihydroxy-2,2-diphenyl) in the ecosphere paid special attention to environmental research. This compound is commonly used as an industrial plasticizer, and is well known for its estrogenic properties. BPA is present in paints, unsaturated polyester resins, plastic food packaging, containers for water, foils used for food storage, and infant feeding bottles. Several studies confirmed significant amount of BPA detected in food containers [46-48].

Potential dangerous effects of BPA for the natural environment are not clear so far. On one hand, BPA cannot be treated as an important pollution factor due to the fact this compound is relatively quickly metabolized and excreted from the body. However, on the other hand, some researchers suggested that BPA is carried by the placenta, where only a part of it is metabolized and excreted, whereas the rest remains in women exposing both the mother and fetus to long-term risk [49-51]. It must be noted that BPA, even at very low concentrations, shows potential estrogenic properties [52,53].

4 Analytics of emerging contaminants of anthropomorphical nature

In the year 2000, the US Geological Survey performed a national reconnaissance of pharmaceuticals and other organic waste water contaminants in ground and drinking water sources [54,55]. In this study, water samples were collected from a network of 47 ground water sites across 18 US States, and 65 organic compounds were analyzed. The most frequently detected compounds were DEET (Diethyltoluamide), an insect repellant (frequency of detection 35%), the aforementioned Bisphenol A (30%), Tri(2-chloroethyl)-phosphate (30%, fire retardant), Sulfamethoxazole (23%, veterinary and human antibiotic), Carbamazepine (20%), Tetrachloroethylene (24%, solvent), 1,7-Dimethylxanthine (16%; caffeine metabolite), and 4-Octylphenol monoethoxylate (19%). Pesticides were identified before as common contaminants in shallow ground water [56], having been found at 54% of 1034 sites sampled in agricultural and urban settings across the United States. Of the 46 pesticide compounds examined, 39 were detected, and the most frequently detected compounds were Atrazine (38%), Desethylatrazine (34%), Simazine (18%), Metolachlor (15%), and Prometon (14%). In Europe, the chemical monitoring of ground water has received somewhat less attention compared to surface waters, and comprehensive monitoring surveys are urgently necessary. However, a few local studies proved that persistent micropollutants like carbamazepine or clofibric acid may enter the ground water nearly un-attenuated by bank filtration of affected surface waters or by infiltration or artificial recharge of treated wastewater into ground water [57,58].

ECs (emerging contaminants) are also increasingly being used as environmental tracers for characterizing sources and processes which may be controlling the occurrence, transport and fate of contaminants in the subsurface [59,60]. When used in combination with groundwater residence time tracers, such as chlorofluorocarbons (CFCs) or sulphur hexafluoride (SF6), these could be powerful techniques for understanding contaminant processes and groundwater vulnerability.

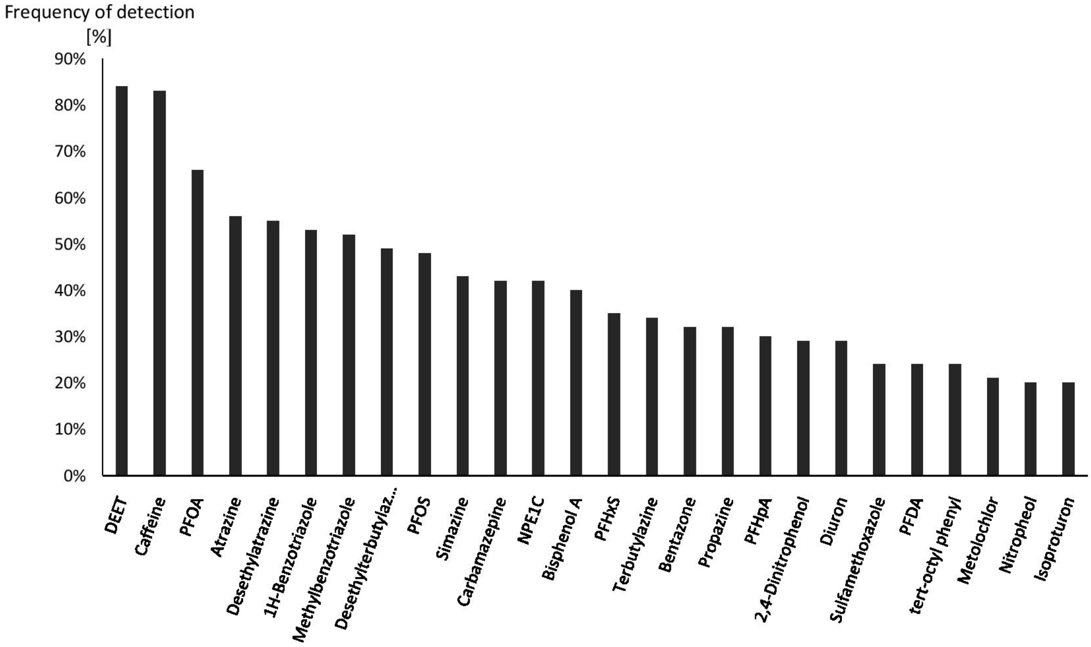

Figure 1: Frequency of detection for compounds present in 20% or more of samples detected by Loos et al. [63] .

Loos et al. [61] report a pan-European reconnaissance for polar persistent organic pollutants in groundwater. In total, 164 individual groundwater samples from 23 European countries were collected and analyzed (among others) for 59 selected organic compounds, comprising pharmaceuticals, antibiotics, pesticides (and their metabolites), perfluorinated acids (PFAs), benzotriazoles, hormones, alkylphenolics (endocrine disrupters), caffeine, DEET, and triclosan. Fig. 1 shows the frequency of detection for compounds present in 20% or more of samples, and Fig. 2 the maximum concentrations detected by Loos et al. [61]. The most relevant compounds in terms of both frequency of detection and maximum concentrations detected were DEET, caffeine, PFOA, atrazine, desethylatrazine, 1H-benzotriazole methylbenzotriazole, desethylterbuthylazine, PFOS, simazine, carbamazepine, nonylphenoxy acetic acid, bisphenol A, perfluorohexane sulfonate terbuthylazine, bentazone, propazine, perfluoroheptanoic acid, 2,4-dinitrophenol, diuron and sulfamethoxazole. In an investigation into the occurrence of perfluorinated compounds in groundwaters of England and Wales in 2006, perfluorinated compounds were detected in 26% (57 of 219) of groundwater monitoring sites, with detectable concentrations of PFOS found at about 14% of sites [62-64].

A review has been published [62], inspired by US research, of the types of EGCs which are beginning to be found in UK groundwater. It discusses the routes by which these compounds enter groundwater, including resistance to wastewater treatment, their toxicity and the consequent potential risks posed to drinking water and the environment. Specific compouns frequently detected include pesticide metabolites, pharmaceuticals including carbamazepine and triclosan, nicotine, food additives and alkyl phosphates. Data from the Environment Agency's monitoring programme for organic pollutants presented in this study indicate that within the 30 most frequently detected compounds there is a significant number of emerging contaminants: atrazine metabolites, caffeine and DEET. Specific compounds with multiple detections include pesticides metabolites, pharmaceuticals including carbamazepine, triclosan, nicotine, food additives and alkyl phosphates [62].

Another paper [4] summarisies the first study to characterize the occurrence of a broad range of ECs (n > 1000) in African groundwater (with a focus on groundwater beneath Kabwe, Zambia). The objectives were to: i) quantify the occurrence of ECs in groundwater sources in urban and peri-urban settings, ii) compare contamination in shallow sources against deep bedrock sources, iii) assess temporal variations in ECs between dry and wet seasons, iv) evaluate relationships between occurrence, land use and localized contaminant risk factors, v) understand the vulnerability of groundwater using ECs in conjunction with residence time indicators and in-situ electrical conductivity data. A total of 27 compounds were identified including the omnipresent DEET, at a median concentration greater than that

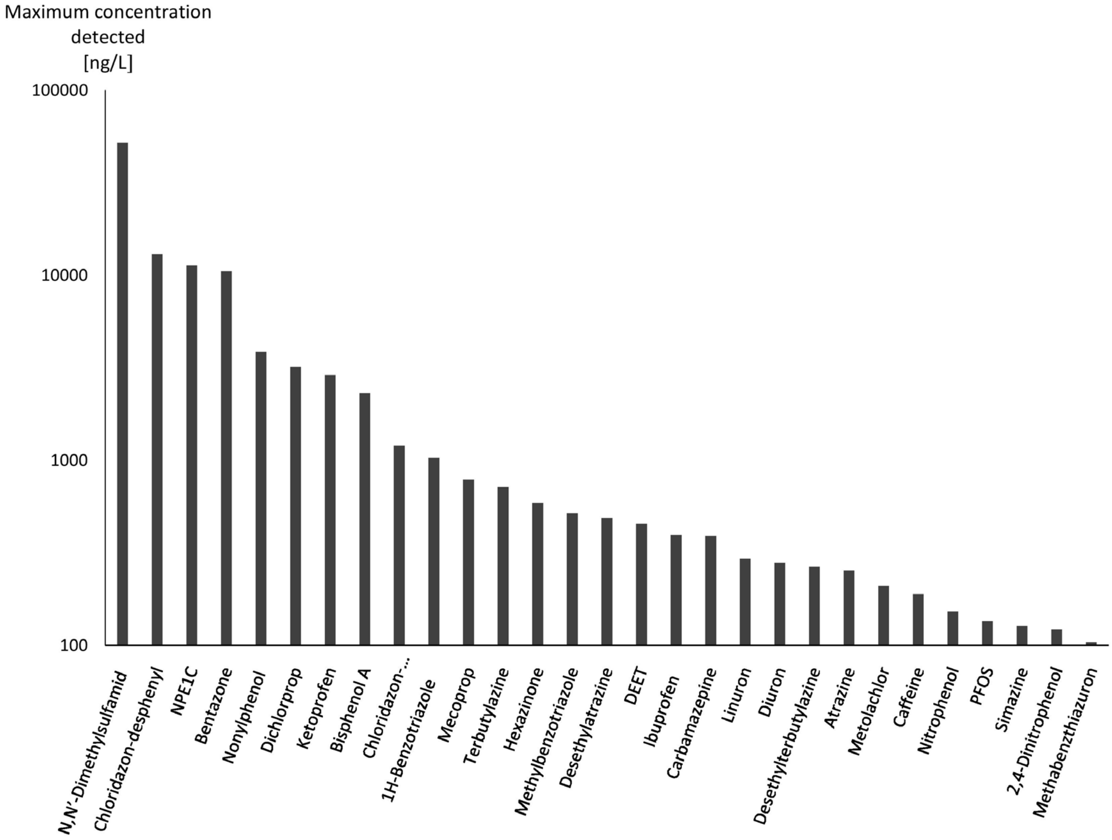

Figure 2: Maximum concentrations for compounds present in 20% or more of samples detected by Loos et al. [63]

observed in other groundwater studies across the globe. Triclosan, THMs, herbicides, insecticides and chlorinated solvents were observed at a limited number of sources. Contamination was most extensive within shallow wells sited in areas of low cost housing, due to inadequate sanitation, household waste disposal, and poor well protection and construction. The compounds detected are not directly linked to human waste and consequently there appears to be no association with sewage disposal in pit latrines in Kabwe. The insect repellent DEET was ubiquitous within groundwater at concentrations up to 1.8 mg L^{-1}. Other compounds were detected in less than 15% of the sources and included the bactericide triclosan (up to 0.03 mg L^{-1}), chlorination by-products trihalomethanes (up to 50 mg L^{-1}), and the surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol (up to 0.6 mg L^{-1}). Emerging contaminants were most prevalent in shallow wells sited in low cost housing areas.

The new challenge of the last decade, both for the technology and waste water treatment, as well as analysis, is the presence of pharmaceuticals in the environment, particularly in aquatic ecosystems. The presence of pharmaceuticals in drinking water represents a real threat to human health. It should be emphasized that the metabolites of drugs and their decomposition products formed in the wastewater treatment or during the treatment of drinking water possibly increase their toxicological properties [65].

As it may be found in the literature, pharmaceuticals are mainly detected in wastewater, effluent from sewage treatment plants, surface water, groundwater and leachate from landfills [66].

One of the major problems faced by the modern science of environmental pollution issues is also related to the common use of antibiotics, both human and veterinary pharmaceuticals. The increase in the production and consumption of antibiotics in the modern world is alarming [67]. Circulation of antibiotics in the nature is due to their incomplete conversion in the human or animal body [68].

5 Non-steroidal inflammatory drugs

Another issue is the question of non-steroidal inflammatory drugs (NSAIDs). This group of compounds includes common pharmaceutical products sold without a prescription, and frequently overdosed. Aspirin, acetaminophen, ibuprofen, diclofenac are just some of the ingredients sold in pharmacies, supermarkets and petrol stations. Until recently it was thought that the biological effect of these substances is conditioned by their high concentration, significantly exceeding the environmental concentrations. In addition, their short duration involving bacterial decomposition in water and the lack of tendency to accumulate also do not increase the risk of this group of compounds to the natural environment.

Recently, a new group of compounds joined the anthropological-based pollutants – these are drugs, in general – intoxicating substances. The legality and availability of drugs is increasing every year. Among others, one may enumerate those available on prescription: amphetamine derivatives, ephedrine, opiates, codeine, as well as illicit drugs, such as cocaine, amphetamines, morphine, cannabis-alkaloids - cannabinoids, opioids (e.g., methadone), etc.

The United Nations Office on Drugs and Crime (UNODC 2011) reported that in 2009–2010 4.5% of the world's population aged 15–64 used cannabis, 1.3% used amphetamines, 0.6% Ecstasy-group stimulants and cocaine 0.5% [69]. According to the European Monitoring Centre for Drugs and Drug Addiction Annual Report 2011, in many European countries amphetamines or ecstasy are the second most commonly used illicit substances after cannabis [70].

Research undertaken in many European and non-European countries shows that the content of psychotropic drugs and their metabolites in the waters of different origins is large and has a close relationship with their intake [71-76]. It was also found that the removal of psychotropic compounds in the wastewater treatment process is incomplete. The presence of both drugs as their metabolites in the water leaving the treatment plants was detected. At the moment, however, there is no data available to assess the environmental risk related with this problem.

Until recently it was thought that environmental estrogens are present in the ecosystem in too low concentrations, so their impact on the environment is low. However, it was found that a variety of xenoestrogenic substances, plenty of their sources and the nonchalance of the users can lead to serious environmental problems. In addition to numerous compounds entering the ecosystem, whose impact on the environment is well known, new chemical substances, biologically active, are more and more enumerated, and their activity is unrecognized. It should be noted that in addition to a wide variety of compounds well recognized, other substances are being released to the environment, for example arising from chemical degradation of the compounds initially introduced. These primary-decomposition products are often characterized by similar or even greater hazard and durability.

6 Illicit drugs

Several studies have recently reported that illicit drugs are detectable in wastewater from municipal sewage treatment plants (STPs) and surface waters [77]. These substances are excreted in urine and feces unchanged or as active metabolites in high percentages after consumption and continuously discharged into domestic wastewaters. Residues of illicit drugs can therefore reach STPs in substantial amounts, escaping degradation, and are then released into surface waters. Environmental concentrations are low, but risks for human health and the environment cannot be excluded. Morphine, cocaine, methamphetamine and ecstasy all have potent pharmacological activities, and their presence as complex mixtures in surface waters may be toxic to aquatic organisms.

Statistics show that around a third of European citizens have tried an illicit drug, while overdose claims the life of at least one citizen every hour [78]. Ever-changing patterns in illicit drug production, demand and supply necessitate a program of frequent monitoring. Independent, objective and timely information on the type, scale and demographics of illicit drug use is essential in order to fully understand drug use and develop better methods and actions to respond to them [79].

The first research on drugs in wastewater (raw and purified) took place in the US in 2004 for amphetamine. In Europe, the first research of this type was initiated in Italy in 2005. This research was concentrated on cocaine and its main metabolite – benzoate ecognine (BE), by means of mass spectrometry [80]. Cocaine together with its metabolites was detected in many countries across Europe, including Spain, Italy, Switzerland, Great Britain, Belgium, Germany, and Ireland. Intoxicating substances were also detected in US and Brazil, as a result of extensive research of 18 sewage treatment plants [81]. Other substances detected in the following years in high concentrations belonged mainly to the group of the drugs available on prescription, such as amphetamine derivatives, opioids, ephedrine, and metabolites of cannabis [80]. A study conducted in Italy was devoted to determining the concentration of the most common drugs and their metabolites in wastewater.

Samples were tested for the presence of: cocaine, amphetamine, morphine, cannabinoids, methadone and their metabolites. Samples were collected from the plant during the whole day and continuously analyzed.

The highest concentration of morphine was reported from 80 to 200 ng dm^{-3}, while cocaine concentration was much lower - about 0.2 ÷ 1 µg dm^{-3}. For other substances, the results were as follows: 10 to 90 ng dm^{-3} for methadone and its main metabolite, 60 ÷ 90 ng dm^{-3} for cannabis derivatives, and less than 20 ng dm^{-3} for amphetamine [82]. Another Italian study underwent a detailed analysis of the river Pad and sewage treatment plants in the villages along the tributaries. The detected level of cocaine was 1.0 ÷ 1.4 ng dm^{-3} in the river, and from 42 to 120 ng dm^{-3} in the basin. Cocaine metabolite level was higher: from 20 to 30 ng dm^{-3} in the samples from the river, and from 390 to 750 ng dm^{-3} in outflows from sewage treatment plants [83]. It has been calculated that the water that enters the river each day may contain 3800 g of cocaine [84].

Recently, many reports estimating illicit drug abuse using ‘sewage epidemiology’ have been published in many European countries, such as Belgium [75,85,86], United Kingdom [87,88], Italy – Florence [89], Spain [90-92], Croatia [76], Switzerland [93], Norway [94], Poland [95-97], Sweden [98], and also in Canada [99] and the United States of America [100-103].

Over the past few years the analysis of drug residues in sewage has been promoted as a means of estimating the level of drug use in communities. Measured drug residue concentrations in the sewage are used to determine the load (total mass) of the drug being used by the entire community. Knowledge of the size or population of the community then allows for the calculation of drug-use relative to population (typically drug-mass/day/1000 inhabitants) which facilitates comparisons between differing communities or populations [104]. The analysis of biomarkers of drug use in sewage has great potential to support and complement existing techniques for estimating levels of drug use, and as such has been identified as a promising development by the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) [105].

In order to estimate levels of drug use from wastewater, researchers attempt first to identify and quantify drug residues and then to back-calculate the amount of the illicit drugs used by the population served by the sewage treatment plants [104]. This approach involves several steps (Fig. 3).

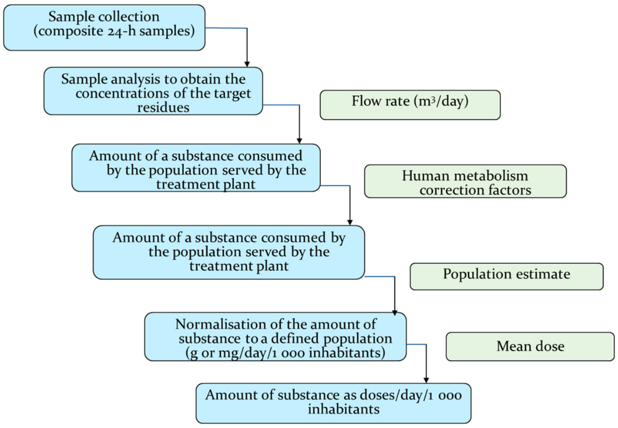

Figure 3: Wastewater analysis approach [104].

In 2010, a Europe-wide network (Sewage Analysis CORE Group – Europe) was established to standardize the approach to wastewater analysis and to coordinate national studies. Following the success of an initial study in 19 European cities [106] a comparable study was undertaken covering 23 cities in 11 European countries in 2012 and 42 cities in 21 European countries in 2013 [107]. This approach made it possible to directly compare illicit drug loads in Europe over a one-week period. This was the first time a European-wide study was performed using a standard protocol and a common quality control exercise while covering multiple countries and years [106]. Raw 24-hour composite samples were collected during a single week in March 2013. These were analyzed for the urinary biomarkers (i.e. measurable characteristics) of the parent drug (i.e. primary substance) for amphetamine, methamphetamine and MDMA. In addition, the samples were analyzed for the main urinary metabolites (i.e. substances produced when the body breaks drugs down) of cocaine and cannabis, which are benzoylecgonine (BE) and THC-COOH (11-nor-9-carboxy-delta9-tetrahydrocannabinol).

The trends and patterns being detected by wastewater analysis are largely, but not completely, in line with the analyses coming from other monitoring tools. Prevalence data from surveys and wastewater analysis both present a picture of a geographically divergent stimulant market in Europe, where cocaine is more prevalent in the south and west, while amphetamines are more common in central and northern countries [105]. Data from established indicators and from wastewater also show that methamphetamine use has been primarily concentrated in the Czech Republic, but is now also present in some other countries [105]. Similarly, both studies based on self-reported drug use and wastewater data point towards the same weekly variations in use, with stimulants such as amphetamine and cocaine being primarily used at weekend music events and in celebratory contexts [108].

Illicit drugs and their metabolites are the latest group of emerging pollutants. Determination of their concentration in the environment (such as water bodies, soil, sediment, air) is an indirect tool to estimate the community level consumption of illicit drug and to evaluate potential eco-toxicological impacts from chronic low level exposure. They enter the wastewater network as unaltered drugs and/or their active metabolites by human excretion after illegal consumption or by accidental or deliberate disposal from clandestine drug laboratories. Reference [109] critically reviews the occurrence and concentration of illicit drugs and their metabolites in different environments (e.g., wastewater, surface waters, groundwater, drinking water, and ambient air) and their potential impact on the ecosystem. There is limited published information available on the presence of illicit drugs in the environment, reports are available mainly from European countries, UK, USA, and Canada but there is a lack of information from the remainder of the world. Although the environmental concentrations are not very high, they can potentially impact the human health and ecosystem functioning. Cocaine, morphine, amphetamine, and MDMA have potent pharmacological activities and their presence as complex mixtures in water may cause adverse effect on aquatic organisms and human health. However, there is no current regulation demanding the determination of occurrence of these emerging pollutants in treated wastewater, surface water, drinking water, or the atmosphere. Thus, critical investigation on the distribution pattern of this new group of emerging contaminant and their potential harmful impact on our environment need immediate attention.

Over the past few years a new technique, based on the analysis of urinary drug biomarkers in sewage, has been developed to complement existing epidemiological studies. This approach has been referred to as ‘sewage epidemiology’ and ‘Forensic Epidemiology Using Drugs in Sewage’ (FEUDS); [110]. The technique, which is effectively a community-scale drug test, has thus far been used in the estimation of drug use by specific populations (i.e. cities) in Europe, North America and Australia [94]. Table 1 presents the analysis of community-wide drug consumption by detection and quantification of specific urinary excretion products in sewage, pairing the drug of abuse with the sewage analyte [94] and a list of countries in which such studies have been performed since 2009 (references in brackets). As summarized in Table 1, there is a correlation among the countries and the drugs under investigation, caused by estimated popularity of the drugs and thus provoked research interest. Alongside developments in wastewater analysis at the general population level, a new technique has been established that involves the collection and analysis of pooled urine from stand-alone portable urinals. This method can detect both traditional drugs and new psychoactive substances, including previously undetected drugs, even at low concentrations [122-125].

Research performed in many European and non-European countries shows that the content of psychotropic drugs and their metabolites in the waters of different origins is large and has a close relationship with their intake [116-121]. It was also found that the removal of psychotropic compounds in the wastewater treatment process is incomplete. In the water leaving the treatment plants the presence of both drugs alone as their metabolites was detected. At the moment, however, there is no data available to assess the environmental risk.

Because the research on the presence of drugs in surface and drinking water has been undertaken for a few last years only, there is no data on the long-term human exposure to low concentrations of these substances. Acute toxicity and unknown changes taking place in the presence of other active substances in the wastewater allow presuming that their presence may have a negative impact on human health in the long run.

7 UV filters

UV filters, designed to provide reasonable protection of the skin against UV radiation and detected mainly in the aquatic environment, recently took more attention of the researchers. The first observations of UV filters were started after detecting the mass extinction of coral reefs along the Australian coast, correlated with crowded tourist spots. Then, similar problems were reported for most of the inland waters: streams, rivers, irrigation canals, lakes, including artificial lakes.

The best known and most commonly used ingredients of UV filters are compounds from the group of benzophenones (BPs), mainly 2,4-dihydroxybenzophenone (BP-1) and 2-hydroxy,4-methoxy benzophenone (BP-3). These compounds act as chemical filters to protect against the adverse effects of ultraviolet radiation impact. This radiation can contribute to the destruction of collagen fibers which in turn can lead to a reduction in immune response. Furthermore, it is also responsible for the formation of free radicals which cause damage to the structure of the proteins which can lead to tumor formation [126].

Table 1: The analysis of community-wide drug consumption by detection and quantification of specific urinary excretion products in sewage.

Country	*Sewage analyte*	*References*
Croatia	Heroin	[76]
	Cocaine	
	Marijuana	
	Amphetamine	
	Ecstasy	
Canada	Heroin	[99]
	Benzoylecgonine (BE)[8]	
	Amphetamine	
	Methamphetamine	
	Ecstasy (i.e. MDMA)[1]	
Poland	Amphetamine	[95-97]
	Methamphetamine	
	MDA (3,4-methylenedioxyamphetamine)	
	MDMA or ecstasy (3,4-methylenedioxymethamphetamine)	
Norway	Ethylsulfate	[112]
	Benzoylecgonine	[111, 112, 118]
	Amphetamine	[118]
	Methamphetamine	
	MDMA[1]	
	Morphine	
Belgium	Ecgonine Methylester	[114, 115, 121]
	Cocaine	[85, 86, 115, 121]
	Benzoylecgonine	
	EME[2]	
	Amphetamine	
	Methamphetamine	
	EDDP[3]	
	MDMA[1]	[115]
Spain	Cocaine	[91, 116, 120]
	Amphetamine	
	Methamphetamine	
	THC-COOH[4]	
	MDMA[1]	
	MDEA[5]	
	MDA[6]	
	Morphine	[116, 120]
	Codeine	
	THC[7]	
	EDDP[3]	
Australia	Cocaethylene	[119]
	Amphetamine	
	Methamphetamine	
	THC-COOH[4]	
	THC[7]	
	MDMA[1]	
	MDEA[5]	
	MDA[6]	
	Morphine	
	Codeine	
	EDDP[3]	
France	Amphetamine	[117]
	MDMA[1]	
Switzerland	Amphetamine	[93]
	Methamphetamine	
	THC-COOH[4]	
	MDMA[1]	
	Morphine	
	Codeine	
	EDDP[3]	
Italy	Benzoylecgonine	[89,102]
	Amphetamine	
	Methamphetamine	
	THC-COOH[4]	
	MDMA	
	Morphine	
UK	Cocaethylene	[87,88]
	Amphetamine	
USA	Cocaethylene	[100-103]
	Methamphetamine	
	MDMA	

(MDMA)[1] 3,4-methylenedioxymethamphetamine, EME[2] ecgonine methyl ester, EDDP[3] 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine, THC-COOH[4] (11-nor-9-carboxy-delta9-tetrahydrocannabinol), MDEA[5] (3,4-metylenodioksy-N-etyloamfetamina), MDA[6] (3,4-methylenedioxyamphetamine), THC[7] (tetrahydrocannabinol), BE[8] (benzoylecgonine)

Fig. 4 shows schematically ways of migration of components of the UV filters into the environment [127].

As follows the scheme from Fig. 4, UV filters are placed directly into natural waters due to discharge from recreational areas and as a result of discharges of wastewater from households and industry. Indirectly, these compounds are excreted into the environment as a result of discharge of waste water from plants involved in cleaning them.

As reported in the literature, UV filters are present in wastewater and natural waters such as seas, lakes, rivers, and in sewage sludge and soil [127,128].

Recently, some research started to estimate estrogenic properties of UV filters [129-131]. As shown in the literature, UV filters, even at low concentrations, may interfere with the endocrine system of mollusks. In higher concentrations these compounds can be toxic to many aquatic organisms [132]. Research conducted on fish species (zebra fish) show that fixed-dose UV-filters (EHMC), even at low concentrations (such as $2.2\ \mathrm{mg\ dm^{-3}}$), can cause significant genetic changes, and affect the transcription of genes involved in the metabolism of hormones in the body. UV filters show also a negative effect in the processes of construction and reconstruction of tissues, the efficiency of the immune system, inflammation and DNA damage [133].

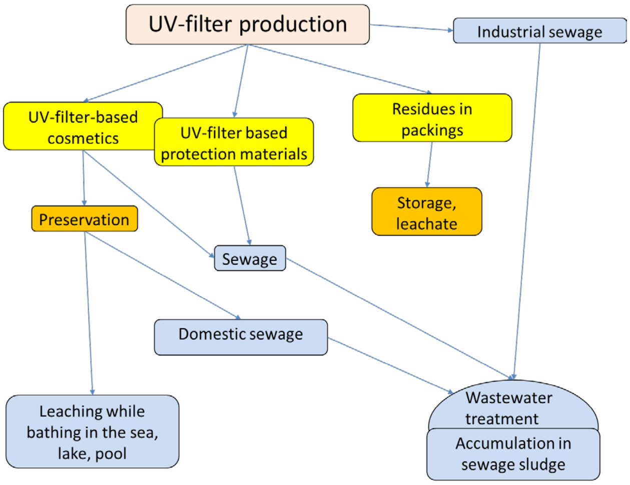

Figure 4: Ways of migration of components of the UV filters into the environment [127].

The negative impact of UV filters on several living organisms (such as rats – uterine hyperplasia, fish Pimephales promelas – 800-fold increase in the level of glycoprotein VTG, egg yolk precursor protein produced by estrogen and estrogenic substances) was demonstrated. Even if the concentrations used for the experiments were much higher in comparison to real environmental samples [132-136], the risk associated with lipophilic properties of UV filters which can therefore be accumulated in the fatty tissues of living organisms, especially long-lived, should be considered. It is also important that the highly lipophilic properties of UV cosmetics enable them to rapidly cross the dermal tissue, which can cause bioaccumulation in the human body. As a result, in a few hours after application to the skin, these UV filters could be detected in the plasma, bile and urine [137]. Furthermore, some of the UV filters have been detected in human milk [138].

UV filters also show a natural possibility of mutual reinforcement due to the presence of some other substances showing potential synergy properties [126]. In addition, these compounds may chemically self-transform after an explosion to UV radiation to other metabolites, potentially comparable to or with even stronger adverse effects on the environment [84].

Numerous attempts to describe the phenomenon of penetration of the UV filter components into different types of water reservoirs have been taken in Switzerland. The research studied and compared concentrations of these compounds in lakes and major rivers, including Lake Zurich and Huttheresee. Lower concentrations of the UV filters were observed in Lake Zurich – from 2 to 29 ng dm^{-3}, Lake Huttheresee was found more polluted with the concentration from 2 to 125 ng dm^{-3} [131]. As a part of another research project, the concentration of UV filters in 10 points along the river Glatt was investigated. Four UV-filter related compounds were detected (listed in descending concentration): BP-4 > BP-3 > 4-MBC > EHMC. BP-3, 4-MBC and EHMC were observed at a concentration of 6 to 68 ng dm^{-3}. The results obtained from the river Glatt test are comparable to the concentration of the UV filters in Swiss lakes. Comparable levels of BP-3, about 27 ng dm^{-3}, were recorded in Spain. UV filters based on benzophenone derivatives have also been detected in similar concentrations in the rivers and lakes of Korea [135].

Another study conducted in France confirmed the mass presence of UV-filter compounds, in mussels and aquatic organisms. The highest observed concentration of OTC in the effluent drains was equal to 270 ng dm^{-3}, while the concentration of EHMC was determined at the level of 100 ng dm^{-3}, and OD-PABA – at 7 ng dm^{-3}. The concentration of the same filters in river water was equal to 1040 ng dm^{-3} for EHMC, 250 ng dm^{-3} for OTC, and 47 ng dm^{-3} for OD-PABA [125]. In Germany, the study was concentrated on four UV-filer related compounds: B-MDM, EHMC, 4-MBC and OTC. Their presence in waters, sediments, mules, and their accumulation in aquatic ecosystems was determined. However, most attention was paid to surface water samples. Measured concentration of any of the tested UV filters did not exceed a value of 4 µg dm^{-3}. Filters were found not only in the waters of the river or in drains, sewage, but also in sea ecosystems and marine waters. The highest concentration in marine waters was detected for 4-MBC – 799 ng dm^{-3} close to the area of popular beaches [139].

The cooperation of the French and Lebanese research institutions has resulted in extensive research of rivers and aquatic environments of the Mediterranean. In 2010–2011, they monitored over 37 sampling points from the region of the eastern part, and 6 places in the western Mediterranean part. Studies were carried out both in the dry and rainy seasons. Research points were arranged as follows: 31 sites were located along the three main Lebanese rivers: Abu Ali, El-Bared and El-Kebir. Six points were located along the coast of El-Mina, their location corresponded to various human activities, such as a commercial and fishing harbor. Finally, 4 points were located in the discharge area of treated sewage treatment plant [140]. Six research points were located in France and in adjacent waters. Three test points were located along the river Lez, another in the coastal lagoons and at the mouth of the sea. Total concentration of UV filters ranged from 12 to 304 ng g^{-1} in Lebanese waters.

Table 2: Determined concentrations of benzophenones in environmental samples.

No	*Compound*	*Sample type*	*Period of sampling*	*Concentration [$\mu g/m^3$]*	*References*
1.	Benzophenone-4	raw sewage	summer	1481	[144]
		river water		849	
		sea water		138	
2.	Benzophenone-3	raw sewage	summer	1195	[145]
	Benzophenone-4			4150	
3.	Benzophenone-3	lake water	cold	35	[127]
			hot	125	
4.	Benzophenone-3	industrial wastewater	higher concentrations – summer, lower concentrations – outside summertime	from 6 to 697	[146]
5.	Benzophenone-3	domestic sewage	higher concentrations – summer, lower concentrations – outside summertime	from 720 to 7800	
6.	Benzophenone-3	river water	spring	300	[147]
7.	Benzophenone-1			1000	
8.	Summary of B3 and B1	raw sewage		from 2700 to 4800	

The results of the French side were much lower and ranged from undetectable levels for research equipment up to 33 ng g^{-3} [141].

Studies on the concentration of UV filters have also been undertaken outside of Europe. Pollution problem is more and more addressed in Asia, Australia and Oceania, where the presence of such substances in the water is extremely dangerous for coral reefs, with particular emphasis on dying corals which are a habitat for countless species of animals. The research in Japan rated the cleanliness of 22 rivers, four sewage treatment plants and 3 lakes. The presence of the UV filters was confirmed in all samples.

In addition to the presence of UVA and UVB filters, water samples were also examined for the presence of UVLS stabilizers. Concentration of all UV filters was equal to 357 ng dm^{-3}, and UVLS stabilizers – 86 ng dm^{-3}. The highest concentration reported for OTC was equal to 266 ng dm^{-3} and a large concentration of HHCB was also detected – 262 ng dm^{-3}.The concentrations for the remaining compounds were as follows: 145 ng dm^{-3} for BZS, 74 ng dm^{-3} for EHMC, 70 ng dm^{-3} for UV-328, and 51 ng dm^{-3} for BZP [142]. Another study of the UVF compounds was carried out in China. Four UV-filter related compounds (BP-3, 4-MBC, EHMC, OTC) have been examined in detail for the input and output of waste water treatment plant in Tianjin, in northern China. All UV filters were detected in each of the samples taken at different times of the year, the highest concentrations were recorded during the warm summer months. The concentrations of all UV filters were similar and ranged from 34 to 2128 ng dm^{-3} [143]. The concentrations depend on the location and time of sampling. For example, in the summertime, especially on a sunny day and in the afternoon, one notices a significant increase of the concentration of diphenylketone derivatives in waters. Table 2 summarizes reported concentrations of the three most commonly used benzophenones in environmental samples, and Table 3 the concentrations of UV filters in the environment and biota [77].

Benzophenones, apart their application for skin protection against the carcinogenic effect of ultraviolet radiation, are also commonly used for products such as body lotions, shampoos, bubble baths, hair sprays, etc. These compounds are used for tyre additions, castings, coatings, pigments, textiles and other products in order to increase their resistance to ultraviolet radiation [147,156-158]. They are also applied for the packaging of synthetic materials, in order to extend the shelf life of stored products, which may be subjected to destruction under the influence of sunlight.

It is evident that, due to the ability to absorb harmful UV-B radiation, benzophenones are the most commonly used components of UV filters all over the world. However, as these compounds can potentially cause skin allergies and are suspected of estrogenic activity (especially benzophenone-3 and its metabolite – 2,4-dihydroxybenzophenone), the European Union

Table 3: Concentrations of UV filters in the environment and biota [134].

Environmental sample	*UV filter*	*Max. Conc. Location Reference [ng/l, mg/kg dw]*	*Location*	*Reference*
Lake water	4MBC	80	Switzerland	[131]
	BP3	125		
	EHMC	19		
	OC	27		
	BM-DBM	24		
	BP3	85	Slovenia	[148]
	EHMC	92		
	Et-PABA	34		
	OC	31		
	4HB	85	Korea	[150]
River water	HMS	345	Slovenia	[148]
	BP3	114		
	EHMC	88		
	OC	34		
	DHB	47	Korea	[150]
Seawater (beach	4MBC	488	Norway	[149]
	BP3	269		
	EHMC	238		
	OC	4461		
Raw drinking water	EHMC	5610	California	[[151]
Raw wastewater	4MBC	6500	Switzerland	[153]
	BP3	7800		
	EHMC	19000		
	OC	12000		
	BP3	6240	California	[151]
	EHMC	400		
Treated wastewater	4MBC	2700	Switzerland	[153]
	BP3	700		
	EHMC	100		
	OC	270		
Swimming pool water	4MBC	330	Slovenia	[148]
	BP3	400		
Fish (lakes)	4MBC	3.80 mg kg^{-1} (lw)	Germany	[155]
	HMS	3.10 mg kg^{-1} (lw)		
	EHMC	0.31 mg kg^{-1} (lw)		
	BP3	0.30 mg kg^{-1} (lw)		
	4MBC	0.17 mg kg^{-1} (lw)	Switzerland	[153]
	BP3	0.12 mg kg^{-1} (lw)		
	EHMC	0.07 mg kg^{-1} (lw)		
	OC	0.02 mg kg^{-1} (lw)		
Fish (rivers)	4MBC	0.42 mg kg^{-1} (lw)^{a}	Switzerland	[154]
	OC	0.63 mg kg^{-1} (lw)^{a}		
Sewage sludge	4MBC	1.78 mg kg^{-1} (dm)^{a}	Switzerland	[152]
	EHMC	0.11 mg kg^{-1} (dm)^{a}		
	OC	4.84 mg kg^{-1} (dm)^{a}		
	OTC	5.51 mg kg^{-1} (dm)^{a}		

requires systematic monitoring of their content in cosmetics [158].

The research results published in the literature confirms that the benzophenones are generally rather efficiently removed from wastewater in biological processes [67,144], with e.g. removal efficiency of benzophenone-3 ranging from 28–30% to 68–96%. However, as typical wastewater treatment usually lacks biological treatment, overall efficiency of the reduction of the presence of these compounds in the wastewater is reduced [144].

8 Conclusions

A wide range of organic micro-pollutants is now being detected in the aqueous environment world-wide. These include nanomaterials, pesticides, pharmaceuticals, industrial additives and byproducts, personal care products and fragrances, water treatment products, flame/fire retardants and surfactants, as well as caffeine and nicotine metabolites and hormones. Many of the compounds are relatively small and/or polar molecules which cannot be effectively removed by drinking-water treatment using activated carbon. Many of these compounds are also toxic or are classed as endocrine disruptors, which in turn requires further research on new technologies for the analysis and purification of sewage and surface water.

A need to control the scale of the migration of all these groups of compounds into the environment points out a new research trend – looking for efficient, economic and environmentally friendly methods for the isolation and precise, quantitative evaluation of their contents in real samples, consistent with the principles of green chemistry. As a consequence, we observe continuous progress in analytical chemistry, in such areas as: preparation of samples for the analysis, improving the speed and selectivity of the separation of analytes (new methods of separation, such as HILIC, UHPLC, 2D-GC, CE in variety of applications and versions), lower limits of detection and limits of quantification, changes in regulations regarding allowable concentrations of selected substances, expanding the range of applications of combined techniques, development of new methods and standard procedures, increasing usage of different methods and analytical techniques in the domain of molecular biology and genetics, miniaturization of measuring instruments, and many more.

Although the idea of estimating e.g. drug consumption based on wastewater analysis looks like a quite attractive proposition, this approach is accompanied by a number of uncertainties. There are various factors that may have important, but currently, poorly understood effects upon the found results and their interpretation. These issues are themselves interesting and further research will undoubtedly be required to enable a better understanding of the usefulness of this approach and better interpretation of the obtained results.

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