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Emerging issues on degradation by-products deriving from personal care products and pharmaceuticals during disinfection processes of water used in swimming pools ☆

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ABSTRACT

The use of disinfection substances in the sanitation and disinfection processes of artificial water used for sports amenities and swimming pools has recently raised some serious concerns. Recreational Water Illnesses (RWIs) can put at serious risk the health of bathers and swimmers due to adverse effects caused by the use of disinfection chemicals, such as chlorine, chloramine, ozone and UV radiation, as well as their by-products. Remarkable documented evidence is available on the impact of Disinfection By-Products (DBPs), such as chloroform and other trihalomethanes, haloacetic acids and chlorophenols, deriving from the oxidation of common organic pollutants dissolved in raw, drinking, waste and artificial waters. Appropriate countermeasures, aimed at avoiding bathers' exposures to these chemicals, have been developed and adopted in public and private structures, also through important scientific contributions and technical provisions issued by the WHO and some national health authorities. On the other hand, it has been demonstrated that high reactive disinfection agents may transform other undesirable chemicals released by bathers, namely pharmaceuticals, sunscreens and other Pharmaceuticals and Personal Care Products (PPCPs) into chlorinated and oxidized compounds and nitrosamine precursors. The first symptoms of potentially adverse health effects on human subjects of these largely unknown by-products should be adequately taken into consideration and investigated.

1. Introduction

The use of disinfection substances in swimming pools, hot tubs and spa are essential tools aimed at safeguarding the health of occasional bathers, professional swimmers and relevant operators [1–3]. Major diseases which may be contracted in artificial recreational waters are due to pathogens of faecal origin, such as bacteria, viruses, fungi, enteric and free living protozoa and other parasites, generally released through human and animal dejections, which may find an ideal environment not only in swimming pools and water park attractions (fountains, water slides and the like), but also in pumps, filters, water piping, external wet surfaces, linen equipment, heating, ventilation, air conditioning, etc. Also algae, which generally do not pose direct risks to humans in artificial waters, may produce feeding biomass for microorganisms and may also endanger bathers through the formation of slippery surfaces. Typical RWIs which may affect swimmers and in particular children and the elderly in poorly managed swimming pools are, among others, enteritis, lung infections and pneumonia, throat sore, dermal infections (*e.g.*, rash and folliculitis), fungal infections of hair, skin, nails and feet, bacterial and viral otitis, conjunctivitis and infections of the urinary tract [1–3]. Harmful microorganisms may conduct part of their life cycles not only in water, but also in the surrounding aerosols and mists, sometimes even favoured by the warm temperature of water, as it is the case of indoor swimming pools, hot tubes and thermal baths, where temperatures up to 40 °C are the rule. The need for preserving the swimmers' health from germ infections became evident in the early years of the 2oth century in the USA, UK and other European countries where sand filtration systems, frequent replacements of pool waters and ozone and UV lamps systems were tentatively adopted [4]. Later on, following the rapid growth of industrial employment of chlorine and its derivatives and the simultaneous development of purifying techniques for drinking water, disinfection experiments involving bleaching powders were conducted. Afterwards, affordable and cost-effective chlorine, chlorine dioxide, calcium/sodium hypochlorite and various dichloroisocyanurate salts were systematically employed [4].

At present, multiple strategies of disinfection coupled with other typical treatment approaches (chemicals for pH control, algal control, stabilizers, flocculating agents) are available. As recognised by most international health authorities [1,2,5], crucial aspects in the sanitization

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and in the disinfection processes of swimming pools are linked to the unavoidable contact of humans with the most frequent disinfection agents and some of their DBPs present in water and in the atmosphere above the water surface. Several chlorinated and brominated DBPs, which are water soluble, volatile and potentially toxic (*e.g.*, trihalomethanes, haloacetic acids, chlorophenols, chlorine vapours) may form when disinfection processes are not properly conducted. These compounds can pose serious risks to the health of swimmers and operators by dermal contact, inhalation and ingestion if effective countermeasures are not adopted and properly monitored [1,5,6].

The recognition of the adverse effects of both pathogenic microorganisms and disinfection chemicals in public and private swimming pools and spa has led to the adoption, in several countries, of legal provisions, guidelines, alerting systems and warning posters which were and are made publicly available wherever artificial water pools are in operation. In recent years, the use of multiple strategies of water disinfection based on high reactive chemicals (such as chlorine, bromine, chloramine and ozone at concentrations of several parts per million) and UV irradiation has attracted the interest of the scientific community on the possible transformation of largely employed PPCPs (medicinal products, sunscreens, fragrances, cosmetics, lotions, etc.) in such reactive environments.

PCPPs are released into water by the skin of swimmers and bathers at varying amounts during the immersion period (suntan lotions in particular). The modification of the original molecules, their inactivation and loss of efficacy, the formation of poorly known by-products, some of which with suspected or proved biological activities, should be carefully considered and investigated. In this paper, a short review on the principal degradation by-products deriving from oxidation and chlorination processes of chemicals in swimming pools is presented.

2. Disinfection processes and disinfection by-products

Oxidizing agents are traditionally used in the sanitization of artificial waters which may contain a multitude of various pathogenic microorganisms, viruses and protozoa. Generally, swimming pools are filled and reintegrated with fresh water (surface and ground water, sea water), water from municipal drinking-water supplies and thermal water. In Italy, water supplied to this purpose must respect the national quality standards of drinking water, with the exception of temperature, whereas inflow water (recycled and reintegrated) and pool water quality must comply with a set of physical, chemical and microbiological parameters subject to specific agreements between central and peripheral health authorities [7]. Table 1 sets forth the key microbiological requirements for swimming pools in Italy [7].

The major biological vehicles associated with RWIs and outbreaks can be traced back to [1,2,8]:

- Faecal origin (human, animals, birds):
  - Various strains of *Escherichia coli*, *Shigella* spp. (bacteria);
  - Norovirus, Adenovirus, Hepatitis A, E, other enteroviruses;
  - *Cryptosporidium*, *Giardia* (protozoa);
- Environmental origin:
  - *Pseudomonas aeruginosa*, *Legionella* spp., *Mycobacterium* spp., *Staphylococcus aureus*, *Leptospira* spp. (bacteria);
  - *Acanthamoeba* spp., *Plasmodium* spp., *Naegleria fowleri* (protozoa);
- Person-to-person contact:
  - *Pediculus humanus capitis* (insects);
  - *Enterobius vermicularis* (nematodes);
  - *Trichophyton* spp., *Epidermophyton floccosum* (fungi).

Other species have been more rarely detected and are not significantly correlated to outbreaks [8]. Table 2 lists the most common pool pathogens and related RWIs [9]. Recently, 107 strains of uncommon germs were isolated and identified in 3 different pools (teaching pool, competition public pool, hydrotherapy pool), thus further pointing out the critical situation of potential risks linked with exposures also in small pool environments and in hydrotherapy activities [10].

Among the various disinfection substances and commercial products involved in inactivation and destruction of dangerous microorganisms, chlorine-based chemicals and, to a lesser extent, the bromine ones, their derivatives and halogenated mixtures are commonly resorted to, particularly in public structures, due to their low cost and convenience of use. As reported by the WHO [1], a great number of chemicals may be present in artificial water aimed at protecting bathers from germ infections. Most of them release and maintain appropriate levels of residual disinfectants in water:

- chlorine group: chlorine gas, calcium hypochlorite, sodium hypochlorite, chlorine dioxide, stabilized compounds, chlorinated isocyanurates;
- bromine group: bromochlorodimethyl hydantoin (BCDMH);
- ozone and UV radiation combined with residual disinfectants, hydrogen peroxide combined with silver and copper ions, biguanide compounds (intended for very small pools);
- other chemicals: basic pH correctors, coagulants, algicides (*e.g.*, quaternary ammonium salts with polymeric chains), anti-scaling chemicals, aesthetic colour correctors.

It is generally recognised that highly reactive disinfection compounds, which are normally present in pools at residual concentrations in the magnitude order of some parts per million [1,2,11], as reported in Table 3, may transform organic matter and pollutants, which are continuously introduced from external sources (bathers and/or animal dejections) or which escape from standard sanitization treatments, into several DBPs which remain in solution or enter the atmosphere above the water surface. Early evidence of transitory or permanent adverse symptoms or lesions in workers, swimmers and children exposed to harmful, toxic and cancerogenic DBPs (*e.g.*, trihalomethanes, chloroform and chloramines) was reported and supported also by epidemiological evidence [6,7,12–14]. Furthermore, health risks for swimmers and operators from potential exposures through pool water ingestion, dermal adsorption and inhalation may be correctly characterized and managed also referring to the existing health-based guideline values and

Table 1
Microbiological requirements for inflow waters and pool waters in Italy [7].

	Inflow water		Pool water	
Bacterial count at 22 °C	≤100	UFC/1 ml	≤200	UFC/1 ml
Bacterial count at 36 °C	≤10	UFC/1 ml	≤100	UFC/1 ml
Escherichia coli	0	UFC/1 ml	0	UFC/1 ml
Enterococci	0	UFC/1 ml	0	UFC/1 ml
Staphylococcus aureus	0	UFC/1 ml	≤1	UFC/1 ml
Pseudomonas aeruginosa	0	UFC/1 ml	≤1	UFC/1 ml

Table 2
Most common pathogenic agents in swimming pools and related RWIs [9].

Pathogenic agent	RWI
Escherichia coli	Enteric infections, conjunctivitis
Legionella pneumophila	Legionellosis, Legionnaire's disease, Pontiac fever
Leptospira interrogans	Haemorrhagic jaundice, aseptic meningitis
Shigella spp.	Shigellosis (bacillary dysentery)
Staphylococcus spp.	Enteric infections, conjunctivitis, skin infections
Streptococcus spp.	Enteric infections, conjunctivitis, skin infections
Pseudomonas aeruginosa	Eye, ear, skin infections
Mycobacteria spp.	Mycobacteria pulmonary disease
Adenoviruses	Pharyngoconjunctival fever, keratoconjunctivitis
Hepatitis A virus	Infectious hepatitis
Norwalk virus	Gastroenteritis
Echovirus	Gastroenteritis
Human papilloma virus	Plantar wart
Cryptosporidium parvum	Cryptosporidiosis (gastroenteritis)
Giardia lamblia	Giardiasis (gastroenteritis)
Naegleria fowleri	Meningoencephalitis (rare, almost always fatal)
Acanthamoeba spp.	Meningoencephalitis (rare, fatal)