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The Persistence and Toxicity of Perfluorinated Compounds in Australia

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This report is intended to be a living document and will be updates as new important information is released.

Contents

1 Summary

"Given the inherent properties of PFOS, together with demonstrated or potential environmental concentrations that may exceed the effect levels for certain higher trophic level biota such as piscivorous birds and mammals; and given the widespread occurrence of PFOS in biota, including in remote areas; and given that PFOS precursors may contribute to the overall presence of PFOS in the environment, it is concluded that PFOS is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted."

PERFLUOROOCTANE SULFONATE RISK PROFILE
Adopted by the Persistent Organic Pollutants Review Committee at its second meeting November 2006

Manufactured fluorinated chemicals are widely used in a variety of consumer goods from non-stick kitchenware to waterproof clothing and even cosmetics, as well as many industrial applications. Produced commercially since the 1950s, two groups of perfluorinated compounds (PFCs), the perfluoroalkyl sulfonates (PFSAs) and the perfluorocarboxylic acids (PFCAs) have raised alarm bells on a global scale. In particular, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been shown to be toxic and very persistent, posing a global contamination problem.

Australian citizens have both PFOS and PFOA in their blood, urine and breast milk. These chemicals are not manufactured in Australia but are found in many imported products and in current stockpiles of old, but still used, fire-fighting foams. Currently there are investigations into environmental contamination with PFOS and PFOA in Victoria at the Fiskville Country Fire Authority's (CFA) training college, at the Williamstown Air Base in New South Wales and at the Army Aviation Centre near the rural town of Oakey, in Queensland.[1] There are likely to be further contamination sites around Australia.

Due to their long half-life in human beings (PFOS 5.4 years and PFOA 3.8 years approx.), there is an increasing risk over time that the exposure will cause adverse effects. A US EPA review concluded that PFOA poses a risk for childbearing women; the estimated exposure range for humans, based on rat studies, having already overlapped with what the US EPA deem as unacceptable for toxic substances.[2] In Europe, PFOA is classified as reproductive toxin and is required to be labelled, "May damage the unborn child". PFOA and PFOS are linked to an increased risk of cancer, endocrine disruption and reproductive harm[3].

Recent research suggests that PFOS concentrations at current population levels may already be causing adverse health impacts,[4,5] which indicates that even these values may be too high. As PFOS and PFOA do not break down, are passed from one generation to the next via breast milk and *in utero*, and have in some cases demonstrated changes in gene expression at very low levels, it is possible that like lead and mercury, there may be no safe level of exposure to PFOS and /or PFOA.

Urgent regulatory action is needed to ensure Australian citizens are protected from ongoing exposures to perfluorinated compounds in consumer products. Special consideration must also be given to ensuring contaminated sites are cleaned up and firefighter's and other relevant worker's health is monitored. The Australian government must immediately ratify and take action on the POPs (Persistent Organic Pollutant) listings on the Stockholm Convention, including the listing of PFOS in 2010.

2 PFOA and PFOS: the dangerous sister chemicals

The most well known use of PFOA is in the manufacture of Teflon, the polymer used in non-stick coatings. PFOA is a very toxic chemical, which has been nominated for listing on the United Nation's *Stockholm Convention on Persistent Organic Pollutants* (POPs), a convention that seeks to eliminate some of the world's most dangerous chemicals. Its sister chemical, PFOS, was also well known in 3M's Scotchguard products. It is an extremely persistent industrial chemical that does not break down.

At the October 2015 meeting of the UN POP Review Committee, the expert group of the Stockholm Convention, committee members concluded that PFOA met all criteria for further evaluation as a persistent organic pollutant; a decision that starts its journey to global elimination. In a consensus decision, the experts agreed that PFOA causes - *"kidney and testicular cancer, disruption of thyroid function and endocrine disruption in women."* [6] In addition, they concluded PFOA was highly persistent, and does not undergo any degradation under environmental conditions.

The Committee also noted that PFOA was detected at sites remote from known point sources indicating that it has the potential for long-range transport via ocean currents and via atmospheric transport of volatile precursors of PFOA, and that it biomagnifies in animals, threatening the food chain. They stated that mothers excrete PFOA via breast milk and transfer PFOA to infants. After giving birth and at the end of breast feeding PFOA re-accumulates in maternal blood. For the next stage of assessment, the Risk Profile, the committee has called for information on the range of PFOA related products on the marketplace including those that will eventually breakdown to PFOA.

PFOS is already listed on the Stockholm Convention as a POP. PFOS is toxic and travels the world in water and air currents, contaminating ecosystems and their inhabitants.

Australian citizens have both PFOS and PFOA in their blood, urine and breast milk. These chemicals are not manufactured in Australia but are found in many imported products and in current stockpiles of old, but still used, fire-fighting foams. The use of these fire-fighting foams has led to extensive contamination of groundwater and soil with PFOS and PFOA affecting rural and regional communities across Australia.

Currently there are investigations into environmental contamination with PFOS and PFOA at the Fiskville Country Fire Authority's (CFA) training college in Victoria, at the Williamstown Air Base, NSW and the Army Aviation Centre near the rural town of Oakey, in Queensland.[7] The serum levels of PFCs in fire fighters were approximately 10 to 15 times higher compared to the general population levels in Australia.[8]

3 How toxic are perfluorinated compounds?

Everyone is exposed to mixtures of perfluorinated chemicals through exposure to dust, indoor and outdoor air, food, water and PFC containing products. PFCs including PFOS and PFOA are found in human blood, urine, breast-milk and babies umbilical cord blood. Due to their long half-life in human beings (PFOS 5.4 years and PFOA 3.8 years approx.), there is an increasing risk over time that the exposure will cause adverse effects.

Mixtures of PFCs have been shown to interfere with the functioning of hormones. Research has demonstrated that at least five PFCs are endocrine disrupting compounds (EDCs) and can affect sex hormones like the estrogen and androgen receptor. In some cases, the mixture effect of exposure to multiple PFCs is more than just additive and researchers emphasised the importance of considering the combined action of PFCs when assessing health risks.[9] Unfortunately, other than PFOA and PFOS, there is little information on the toxicology and health impacts of the suite of fluorochemicals people are exposed to.[10]

A US study analysed PFC levels and the menopausal status of 2,732 women between the ages of 20 and 65 and found that women with higher levels of PFCs had earlier menopause compared to women with the lowest levels and women with higher levels of PFOA and PFOS were also slightly more likely to have had a hysterectomy. [11]

Other studies have demonstrated a relationship between prenatal exposure to PFCs and adiposity (obesity) in children born to women who lived downstream from a fluoropolymer manufacturing plant. Higher prenatal serum PFOA concentrations were associated with greater obesity at 8 years and a more rapid increase in the body mass index (BMI) between 2-8 years.[12] A study of 815 children from the National Health and Nutrition Examination Survey 1999–2008 found an association between serum PFOA and PFOS levels and dyslipidemia (abnormal amount of cholesterol and/or fat in the blood). Dyslipidemia in children is associated with accelerated atherosclerosis (disease of the arteries) and earlier cardiovascular disease development. A significant association was found in adolescents, even at the lower "background" exposure levels of the US general population.[13]

Based on the data of 3,974 adults sampled in the US National Health and Nutrition Examination Survey (NHANES), researchers concluded that higher concentrations of serum PFOA and PFOS are associated with current thyroid disease in the general adult population.[14]

In laboratory animals, PFOS has caused testicular and pancreatic tumours, reproductive and developmental impacts, neurotoxicity and immunotoxicity,[15] as well as affecting the liver.[16] PFOA is a reproductive toxin causing increased mortality in rat pups. It is also a developmental toxicant with prenatal exposure to PFOA causing significant delays in mammary developmental in the female offspring.[17]

The US EPA review concluded that PFOA poses a risk for childbearing women; the estimated exposure range for humans, based on rat studies, having already overlapped with what the US EPA deem as unacceptable for toxic substances.[18] In Europe, PFOA is classified as reproductive toxin and is required to be labelled, "May damage the unborn child".

Both PFOA and PFOS suppress immune responses in adult mice [19] and exposed humans. Elevated levels of PFOA and PFOS have also been associated with significant changes in clinical markers of immune and inflammatory responses.[20] Elevated exposures to PFCs including PFOA and PFOS were associated with reduced immune response to routine childhood immunizations in children aged 5 and 7 years [21] while a reduction of the early immune response to booster vaccination in healthy adults has also been observed supporting the previous findings of PFCs immunosuppression in humans. [22]

The mounting evidence that shows immune suppression occurs at serum concentrations below, within, or just above the reported range for humans and wildlife suggest a potential risk for altered disease resistance. The risk of immune effects for humans and wildlife exposed to PFCs must not be discounted, especially when bioaccumulation and exposure to multiple PFCs from multiple sources are considered.

PFOA has been shown to affect the expression of genes[23,24], while other researchers have demonstrated that PFOA has 'genotoxic' effects[25] on human liver cells.[26] Genotoxic chemicals damage the genetic information within a cell, which can cause mutations and lead to cancer. These chemicals may have no safe level of exposure. The US EPA's expert committee recommended that PFOA be considered 'likely to be carcinogenic to humans.[27]

Following the class action between DuPont (a manufacturer of Teflon which contains PFOA) and US residents in the vicinity of a major contamination incident, the jointly established *C8 Science Panel* concluded that PFOA can cause kidney cancer, testicular cancer, ulcerative colitis, thyroid disease, pregnancy-induced hypertension and medically diagnosed high cholesterol in humans.[28]

To assess health risks from environmental contamination with PFCs, all PFCs should be included in monitoring and their human exposure assessed. More research studies on toxicity, bioaccumulation, carry-over rates and exposure pathways for the other approximately 1000 PFAS are needed in addition to the gaps of PFOS exposure pathways. [29]

4 Perfluorinated compounds in the Australian population

People and animals are exposed to PFCs via food, drinking water, direct contact with products and exposure from indoor and ambient air. PFCs remain in the human body for many years, accumulating primarily in the blood, kidneys and liver. Most Australians have accumulated perfluorochemicals (e.g. PFOS and PFOA) in their bodies.

The UN PFOS risk profile reports, *"Pooled serum samples from 3802 Australian residents, collected 2002-2003 and divided in relation to age, gender and region, were analysed for perfluoroalkylsulfonates, perfluoroalkylcarboxylates and PFOSA. PFOS and PFOSA were quantified in all pooled serum samples with a total range of 12.7-29.5 ng/ml (mean 17.2 ng/ml) and 0.36-2.4 ng/ml (mean 0.81 ng/ml), respectively."*

When compared to monitoring results from around the world, concentrations of PFOS and PFOA in the Australian population in 2010-2011 are similar or higher than our overseas counterparts. Concentrations in Australian women of child-bearing age are almost twice that found in pregnant women from Germany and PFOS and PFOA concentrations are 1.5 and twice those found in adults from the USA.[30]

PFOS and PFOA concentrations have been decreasing in Australian adults[31], most likely due to the decline in global use of the chemicals since 2002. PFOS serum levels in 2008/09 ranged from 5.3–19.2 ng/ml and declined to 4.4–17.4 ng/ml in 2010/11. However given the latest research (see below) on endocrine disruptors these levels may still be dangerously high. PFOA was the next highest concentration at 2.8–7.3 ng/ml (2008/09) and 3.1–6.5 ng/ml (2010/11). All other measured PFCs were detected at concentrations <1 ng/ml with the exception of perfluorohexane sulfonate, which in 2010-11 was detected at 1.4–5.4 ng/ml. [32]

Perfluorinated compounds in Australian firefighters

A 2014 study of 149 Queensland firefighters detected multiple PFCs in their serum. The three most prevalent and detected in all samples were PFOS, perfluorohexanesulfonic acid (PFHxS) and PFOA. Their serum levels of PFOS were approximately six to ten times higher than those found in the general population in Australia. The median/mean level in firefighters was 66/74 ng/mL compared to 12 ng/mL (mean) and 6.8 (median) ng/mL in the general population in Australia. The serum levels of other PFCs like PFHxS in firefighters were approximately 10 to 15 times higher compared to the general population levels in Australia. Even ten years after the phase out of 3M AFFF Industrial Fire Fighting Foam, PFOS serum levels remained above 100 ng/mL and 200 ng/mL in 27% and 3% of the participating firefighters, respectively.[33]

5 Is there a 'safe' level for perfluorinated compounds?

In 2006, the Biomonitoring Commission of the German Federal Environmental Agency established preliminary reference values for PFOA and PFOS in plasma of children and adults. They recommended a maximum permissible serum level for PFOA of 10 µg/l for all groups[34]. For PFOS, it recommended 10 µg/l for children at school beginner age, 15 µg/l for adult females and 25 µg/l for adult males.[35,36]

Recent research suggests that PFOS concentrations at current population levels may already be causing adverse health impacts,[37,38] which indicates that even these values may be too high. A recent study[39] argues that the mean serum levels of PFOS of 14.1 ng/ml are associated with impacts on DNA methylation, suggesting that PFOS may be epigenetically active.[40] Methylation modifies the function of the DNA, typically acting to suppress gene transcription, which in turn may be associated with the development of cancer.[41]

In 2014, the US EPA released a draft[42] of its proposed new reference dose for PFOS of 0.00003 milligrams/kilogram/per day based on developmental toxicity and adverse liver effects. This would be an estimate of how much a person can safely consume daily over a lifetime.

The proposed reference dose for PFOA is 0.00002 mg/kg/day due to adverse changes in the liver linked to developmental effects and adverse changes in the kidney. That proposed reference dose would translate to a legal limit for PFOA of 0.1 ppb in drinking water. While a significant reduction on current advisory level of 0.4ppb, it is dismissed by some researchers as not protective enough of human health, based on new research. These proposed changes to the reference dose have been criticised by state regulators for EPA's failure to consider infant and neonatal exposure levels to two perfluorochemicals (PFCs).[43]

The US state of New Jersey has set their own advisory level for PFOA in drinking water of 0.04 ppb – ten times more protective than EPA's advisory level, but still well above researchers, Grandjean and Clapp 2015 recommendation of 0.001 ppb (based on a serum concentration of 0.1 ng/mL).[44] They argue that the experimental studies the regulatory agencies have relied upon so far have been superseded with more recent studies. Using the data from a recent study of immunotoxicity in children and assuming a linear dose-dependence of the effects, the Benchmark Dose Level (BMDL) is calculated to be approximately 1.3 ng/mL for PFOS and 0.3 ng/mL for PFOA in terms of the serum concentration. Applying an uncertainty factor of ten to take into account individual susceptibility, the BMDLs would therefore result in a reference dose serum concentration of about or below 0.1 ng/mL.[45]

As PFOS and PFOA do not break down, are passed from one generation to the next via breast milk and *in utero*, and have in some cases demonstrated changes in gene expression at very low levels, it is possible that like lead and mercury, there may be no safe level of exposure to PFOS and /or PFOA.

6 Perfluorinated compounds in the environment

PFCs are released into the air and water from waste sites, manufacturing facilities, sewerage treatment works and fire-fighting operations. They migrate out of consumer products such as all-weather clothing, carpets and camping gear into the air, household dust, food, soil, as well as ground and surface water.

PFCs are extremely persistent in the environment and travel the globe via air and water currents. In the air, volatile PFCs (eg polyfluorinated fluorotelomer alcohol (FTOH) and sulfonates) are transported thousands of kilometres and others are carried by suspended particulate matter, which is eventually washed out and deposited in rain and snow. PFCs are also found in water, soil and wildlife and now contaminate every ecosystem in the world from the remote Arctic to the tropics. In recent sampling of snow in remote locations and water from mountain lakes, PFCs were present in nearly all the samples.[46] These data include short chain PFCs, which industry is increasingly using, arguing that they are less harmful than long chain PFCs like PFOS.[47] Unfortunately, like many of the PFCs, there is a dearth of information on toxic effects of short chain PFCs, however, their detection in remote places is of concern, and there are indications that some of the new PFCs are as hazardous as their predecessors.

PFOS has shown no evidence of degradation in the environment [48] and the results of various degradation tests and field monitoring data support the conclusion that no biodegradation of PFOA occurs either.[49] Additionally many PFOA-related substances (eg fluoropolymers) can degrade to PFOA under environmentally relevant conditions. PFOS and PFOA bioaccumulate in fish, birds and mammals with concentrations increasing further up the food chain.

In Australia, PFCs have been found in drinking water collected from 34 locations including capital cities and regional centres. PFOS and PFOA were the most commonly detected; 49% and 44% of all samples respectively. While the maximum concentration in any sample was for PFOS with a concentration of 16 ng /l, the second highest maximums were for PFHxS and PFOA measured at 13 and 9.7 ng/l.[50]

Discharges from wastewater treatment plants (WWTPs) are point sources for PFCs to the aquatic environment. In Australian water reclamation and recycling plants PFOS, PFOA, perfluorohexanesulfonate (PFHxS) and perfluorohexanoic acid (PFHxA) are the most frequently detected PFCs and only those recycling plants using reverse osmosis (RO) technology have been shown to reduce PFC concentrations to below detection and reporting limits (0.4–1.5 ng/l). [51] In an Australian study of leachate from landfills, evaporation and aeration ponds, PFOA was found in every sample. (0.5 - 0.88ug/l) with 6 samples returning measurements of PFOA greater than 0.5ug/l. [52]

Environmental PFC Contamination

The use of PFCs, particularly in fire-fighting foams has been linked to environmental contamination of groundwater in Germany, Sweden, the US[53] and Australia. In 2006 in Sauerland, Germany PFOS contamination of water, pasture, forage and animal products occurred from industrially contaminated biosolids applied to land, while in 2007 there was broad scale contamination of groundwater with PFOS from firefighting foams occurring in Düsseldorf, Germany. In 2013 in Italy, surface, groundwater and tap water were found to be contaminated with PFOS, downstream from a PFAS production plant. Since biodegradation and adsorption of PFOS and PFOA are not known to occur in the aquifers and soils, these are transported at nearly the same rate as groundwater, [54] with the concentrations decreasing only with distance from the source due to diffusion and dispersion.

Currently in Australia, there are investigations into PFC contamination from their use in fire fighting, and fire and rescue training, for example Fiskville Country Fire Authority's (CFA) training college in Victoria, NSW Williamstown RAAF Air Base and the Army Aviation Centre near the rural town of Oakey, in Queensland.[55] Other similar contamination sites are being investigated around Australia.

In 2015, the CFA training base at Fiskville was shut down permanently after tests showed PFOS contamination of the base's water supply. Tests have also showed high levels of the toxic chemical in the fire training area and others areas at the site. The results of 550 tests showed PFOS levels in water as high as 50 micrograms per litre above international guidelines. A farmer adjacent to the site was forced to cease selling animal produce after PFOS was found in the soil and sheep. High levels were also found in the farmer's blood and that of his children.[56]

In NSW, the Australian Defence Force has informed the NSW government that the Williamtown site contains high concentrations of PFOS and other PFCs.[57] The chemicals contaminate not only the RAAF site but also the groundwater under the site and adjacent land and may represent a serious risk to Tomago sands, an important drinking water catchment site situated close to the Williamtown base. Surface water samples have also been found to contain PFOS while ground water and fish from the local creeks were tested for PFOS and were found to contain high levels resulting in an indefinite ban on commercial fishing.[58]

In Queensland from 1970 to 2005, the Australian Defence Force (ADF) regularly conducted fire-fighting drills at the Oakey Airbase, using a PFC based fire-fighting foam. Following an environmental audit of the area in 2010, further tests were conducted in 2014, which confirmed that the contamination had spread beyond the base into water bores used by local land holders and Oakey Creek. PFOS and PFOA contaminated groundwater has been detected several kilometres to the west and southwest of the base. Residents have been told that of the 112 bores tested by Defence in the Oakey area, 42 bores had levels, which exceeded the health advisory drinking limit. The ADF has advised local residents not to drink their bore water or creek water. Queensland Health is understood to be advising residents not to eat eggs or drink milk from animals raised within the contamination zone, as well as avoiding fish caught in nearby creeks. Blood tests of Oakey residents have returned very high PFC levels estimated to be more than 40 times the national average. The ADF has not provided compensation for loss of income or other losses due to the contamination to Oakey business owners/operators. [59]

The Department of Defence (DOD) has also initiated a review of DOD sites based on the known prevalence of the use of Aqueous Film Forming Foam (AFFF) and environmental factors such as groundwater use and hydrogeological conditions. As a result RAAF Base Pearce in West Australia, RAAF Base East Sale in Victoria and HMAS Albatross in NSW are now prioritised for PFOS/PFOA contamination investigations beginning in March 2016. RAAF Pearce has already been the subject of trials to treat PFOS/PFOA contaminated wastewater in collaboration with The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) since 2011. The remediation program is no longer operational. It is expected that significant levels of PFOS and PFOA will be found to contaminate soils at RAAF Pearce where fire fighting practice was undertaken and waste water stored. The degree and extent to which underlying groundwater has been contaminated will be determined during investigations in 2016.RAAF Pearce has operated since 1939 and AFFF has been used at the site between the 1970's and the 2000's. It is situated on a 1000 hectares in a semi-rural area 35 kilometres north northeast of Perth next to the town of Bullsbrook with 4300 residents.

In October 2015, an Ohio woman was awarded $1.6 million in compensation after a jury ruled that PFOA from US company DuPont plant contaminated drinking water and contributed to her development of kidney cancer[60]. This was just the first of many cases against Dupont. Dupont is facing the litigation from an additional 3,500 residents near one of its plants in West Virginia who have also accused the company of contaminating their drinking water with PFOA, resulting in sickness including cancer.

The 2015 *Madrid Statement* on Poly- and Perfluoroalkyl Substances (PFASs) signed by scientists and environmental health specialists from across the globe called for urgent action noting: *"PFASs are highly persistent, as they contain perfluorinated chains that only degrade very slowly, if at all, under environmental conditions."* [61]

7 International regulatory responses

In 2000, the Organisation for Economic Cooperation and Development (OECD) undertook a hazard assessment on PFOS and its salts, concluding that the persistence of PFOS in the environment, its toxicity and bioaccumulation potential indicated cause for concern for the environment and human health.[62]

In 2002, under pressure from the United States Environmental Protection Agency (US EPA), the major manufacturer of PFOS and its precursors, 3M, ceased production. Canada prohibited the manufacture, use, sale, offer for sale and import of PFOS and related substances. In 2006, the European Union adopted a resolution restricting the marketing and use of PFOS and related substances. [63] The US EPA severely restricted the use of PFOS and other perfluoroalkyl substances (PFASs) to uses where no safer alternative is available[64].

In 2010, PFOS was formally listed on the United Nation's *Stockholm Convention on Persistent Organic Pollutants*, a convention for some of the world's most dangerous chemicals. Its listing on Annex B permitted some limited ongoing uses. Work by the conventions scientific and technical committee continues to phase out the remaining uses. For instance, in May 2015, the Stockholm Convention's conference of parties removed a further six of previously permitted uses. Despite being a signatory to the Convention, Australia has not yet ratified the listing of PFOS.

In October 2015, PFOA was nominated for listing on the United Nation's *Stockholm Convention on Persistent Organic Pollutants*. DuPont had agreed to phase out production of PFOA by 2015.

8 Conclusions

Urgent regulatory action is needed to ensure Australian citizens are protected from ongoing exposures to perfluorinated compounds in consumer products, in food and drinking water. This requires:

- Priority phase out of all perfluorinated compounds in consumer products and immediate cessation of the import and use of PFOS and PFOA and those products that degrade to PFOS and PFOA.

- During the phase out period perfluorinated compounds should be labelled to inform consumers, users and waste managers.

- Particular attention should be given to the waste phase of perfluorinated compounds with national regulators ensuring access to non-combustion destruction technologies for PFC treatment.

- Investigation and remediation of environmental contamination is long overdue and regulatory agencies should ensure contaminated sites are cleaned up and fair and equitable compensation processes for affected communities are initiated.

- Special consideration must be given to the health and well-being of firefighter's and other affected workers. An immediate recall of PFOS based fire-fighting foams should be undertaken and an inventory of all PFC based foams commenced.

- Australia must immediately ratify the listing of PFOS.

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9 Endnotes

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1 Department of Defence, Oakey - Army Aviation Centre - Groundwater Investigation Project. http://www.defence.gov.au/id/oakey/Documents.asp

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