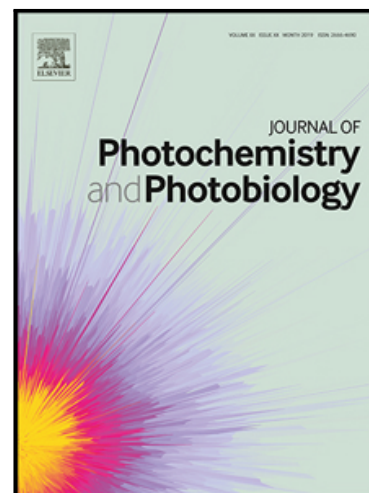


## Journal Pre-proof

Measuring oxidative damage to human hair from solar radiation and pollution: A critical review

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## Highlights

- Solar radiation, with trace metals and air-borne pollution, damages hair fibres
- Solar wavebands affect fibre components in different ways
- Protein and lipid oxidation are common, causing structural breakdown
- Fibre changes include reduced strength, cuticle erosion and poor combability
- Study methodologies simulating realistic exposure levels vary, but are mostly *ex vivo*
- UV filters and antioxidant treatments are common strategies to limit hair damage

Journal Pre-proof

# Measuring oxidative damage to human hair from solar radiation and pollution: A critical review

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## Abstract

Human scalp hair evolved to protect the brain and scalp from environmental factors such as solar radiation and to provide thermoregulation. Whilst the evolutionary drivers for this protective function have diminished,

ongoing global industrialisation has caused concerns about the deleterious effects of solar radiation and environmental pollution on hair. This critical review evaluates published data on the effects of solar radiation on human hair, alone and in combination with pollution (air- and waterborne). The majority of data were generated via *in vitro* experiments in which hair samples were subjected to defined artificial solar radiation and pollutant exposure. Protein and lipid oxidation were the main synergistic oxidative reactions taking place in hair fibres due to solar radiation exposure and in the presence of pollutants and trace metals. UVB radiation mostly impacted the hair cuticle, whilst combined UVA and visible spectra impacted the cortex. Light coloured and bleached hair incurred the greatest damage, whilst dark hair types are less affected. In addition to chemical analytical techniques, oxidative damage to the cuticle was evidenced by scanning and transmission electron microscopy, whilst mechanical fibre measurements were used to infer loss of cortex integrity. In conclusion, whilst solar radiation is the most significant factor, trace metals, air-borne pollution, and the application of products and styling techniques also play a role in hair degradation. These factors could also be referred to as “hair exposome”, and hair protection strategies considered according to the combination of hair characteristics and specific exposome exposure.

**Keywords: Solar radiation, UV radiation, pollution, trace metals, hair damage, oxidative hair damage, exposome**

## **1. Introduction**

Hair is one of two uniquely mammalian features; the other being the mammary glands for milk production [1]. It is found all over the human body apart from areas of glabrous skin. The evolutionary role of hair has been one of protection, acting as a shield from solar radiation (SR) and as a thermal insulator to the head [2]. However, throughout human history, hair has also held a role in both social communication and the expression of cultural identity and personal style [1]. Over time, the relative importance of the protective function of hair has been superseded by the social and cultural significance and with the increasing use of various colour and shape-altering treatments and styling devices, a need to safeguard the hair and to preserve its appearance and longevity has emerged. From a photobiological perspective, human hair represents a complex keratinised substrate containing endogenous chromophores and lipids capable of undergoing light-induced oxidative reactions.

### *1.1. Human hair as a photobiological substrate*

Hair fibres are complex, multilayered structures consisting of three subsections made of keratinised cells: a cuticle, the outermost layer, the cortex, and the innermost section, the medulla [3]. The cuticle is composed of flat, overlapping cells, most commonly reported to range between 5 and 10 layers, and serves as a protective barrier, imparting hydrophobicity and influencing aesthetic hair properties such as shine [4]. Each cuticle cell comprises three layers: the A-layer, the exocuticle and the endocuticle, with a combined thickness of approximately 5 microns [5]. A thin membrane, the epicuticle, covers the outer surface of the cuticle cell. It is made of a protein layer bound by thioester linkages to a single layer of 18-methyl-eicosanoic acid (18-MEA). The A-layer and exocuticle, rich in sulphur, exhibit strong protein cross-linking, particularly in the

A-layer, which has a higher cystine content [5,6]. Spectroscopic analyses have shown that cuticle cells exhibit signals consistent with  $\beta$ -sheet protein conformations [6,7]. The cortex makes up the majority of the structure of the shaft, with estimates varying between 80 and 90% of the shaft's total weight [1]. It plays a crucial role in providing strength and elasticity to hair. It consists of elongated cells containing  $\alpha$ -helical proteins embedded in amorphous proteins characterised by high levels of disulphide bonds. The  $\alpha$ -helical proteins are organised into tightly packed groups of 32, thus conferring hydrophobicity to these areas of the cortical cells. The cortex structure contributes significantly to the hair's overall mechanical resilience [4]. However, studies report that thermal and chemical treatments of hair cause the transformation of  $\alpha$ -helical structures in the cortex to  $\beta$ -sheets [8,9]. Within the cortex cells, melanosomes of circular or oval shape and various sizes are distributed, containing varying amounts of the two types of melanin: eumelanin (dark/black) and pheomelanin (red), which gives hair its colour [4]. By absorbing and dissipating UV radiation, melanin functions as an intrinsic photoprotective chromophore within the hair shaft [4,7–11], thus preserving its cellular and morphological integrity.

The cell membrane complex (CMC) of the human hair comprises two lipid layers ( $\beta$ -layers), each adjacent to and partially bound to the respective cell membranes, and a central proteinaceous  $\delta$ -layer, which provides the intercellular adhesion [4,10].

Proteins in hair are highly susceptible to oxidative attack due to high reaction rate constants with reactive species, leading to modifications of both amino acid side chains and the peptide backbone [11]. Specific amino acid residues exhibit distinct reactivity profiles, with sulfur-containing residues such as

cystine and methionine, as well as aromatic residues such as tryptophan, being particularly prone to oxidation, nitration, and cross-linking reactions [12]. Additionally, protein functional groups can react with lipid peroxidation products originating from the CMC, forming secondary reaction products and cross-linked structures [12]. Hair proteins also exhibit these reactivities; consequently, exposure to environmental factors and cosmetic treatments can lead to significant deleterious effects on perceived hair quality, alongside measurable structural degradation and mechanical weakening. These factors collectively constitute a hair-specific exposome and understanding how they interact extends the photochemical and photobiological insights towards the development of practical hair protection and management strategies.

### *1.2. Aim of Review*

This article reviews original research from the past 25 years, focusing on the detection and quantification of SR-induced damage to human hair. The review also includes airborne pollution as a photochemical sensitiser and trace metals in water as amplifiers of oxidative reactions under UV exposure. The analytical approaches to measuring the extent of photochemical degradation of hair and its effect on hair morphology and discernible hair quality are also discussed. Finally, these findings are combined via the discussion of a hair exposome model and relevant protection scenarios and strategies.

## **2. Methods**

### *2.1. Search strategy*

Two comprehensive literature searches, one focused on hair and SR and another on hair and pollution, were performed of the following indexing and

publishing databases: ScienceDirect, PubMed, Wiley Online Library, MDPI and the Journal of Cosmetic Science (Society of Cosmetic Chemists, USA). At the time of the literature search, which concluded in December 2025, the authors did not identify any review papers that jointly investigate the effects of solar radiation and key environmental factors on human hair.

*Inclusion and exclusion criteria.*

The following inclusion and exclusion criteria were applied in the selection of studies:

- i) Original research articles published between 2000 and 2025 in English were included, provided they did not focus exclusively on commercial cosmetic preparation evaluations.
- ii) Skin, scalp and hair follicle, and general human health studies were excluded, as were studies involving animals.
- iii) Book and other review papers were excluded. Exceptions were made for one seminal book, outlining the hair fibre structure and composition of direct relevance to the substance of the review, and one book chapter from 2001, the first text dedicated to examining thoroughly the impact of SR on hair chemistry and morphology.

This approach was designed to prioritise recent, original, and methodologically innovative research and to maintain focus on photochemical and photobiological implications of SR on hair.

### **3. Results and discussion**

A total of 40 peer-reviewed articles which met the above criteria were identified and included in this review. The key experimental details and outcomes

have been extracted and presented in *Supplementary Table 1*. The findings of all studies have been presented under several topics addressing the photochemical properties of the different hair morphological components and the impact of the hair exposome factors on these. The methodologies applied for assessing these are also summarised and critiqued.

### 3.1. *Spectral penetration and exposure context*

The most common experimental design involved irradiating hair in a laboratory with a solar simulator with optical filters applied as appropriate (optically filtered xenon lamp) or with mercury vapour lamps emitting in specific wavelengths. Beyond the wavelength, various units were used to report the quantity of light applied. The most common outputs reported were: radiant energy (J) (related to the light source); irradiance - the power of the emitted radiance over a set unit area or the object ( $\text{W m}^{-2}$ ); radiant exposure (dose) – the total energy dose delivered to the object over the set time period [13]. A small number of studies were based on the analysis of hair exposed to ambient light.

Several studies assert that UVA+Visible+IR bands penetrate deeper into the hair shaft, reaching the cortex, whereas UVB primarily penetrates the outer cuticle [14–19]. UVB radiation was linked to protein degradation in a variety of irradiated hair tresses, which lost protein compared with unirradiated controls [8,12,14]. UVB radiation was also specifically observed to cause significant damage to the hair cuticles, including changes in cuticular edges and detachment [18]. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are employed, in conjunction with chemical analyses, to demonstrate the structural disruption to different morphological parts of the hair following hair fibre irradiation [18,20]. The results suggested that UVA radiation

penetrated deeper into the hair shaft, resulting in more pronounced biochemical changes, including proteins and lipids.

However, the melanin in the cortex absorbs SR radiation, thus mitigating the effects on other proteins, with darker hair being more protected [16]. Consequently, the cuticle layer emerges as the region most highly susceptible to damage, being devoid of melanin and the initial point of penetration for incident radiation.

Different investigators utilised different regions of the spectrum in their laboratory experimental protocols [14,15,17–19,21–41]. For details on spectral exposure and the types of solar simulators, refer to *Supplementary Table 1*. This lack of consistency in exposure makes comparisons between studies challenging. Most laboratory studies acknowledged high experimental doses of radiation exposure, but did not report the light simulator's intensity, irradiance and wavelengths together, mostly one or the other. Difficulties were encountered with the interpretation of 'real-world' studies too, with exposure often reported in hours only [14,29,35,42]. As these were commonly linked to tropical and humid locations (e.g. Florida, Brazil), it is not yet known if exposures in moderate climates translate to comparable patterns of hair damage and degradation.

Despite the many different methodologies, in all cases, longer exposure and higher SR doses were associated with increased hair damage. Specific mechanisms were proposed based on the chosen chemical markers and often in combination with fibre surface or whole fibre characterisation. More recent studies (discussed in detail in section 3.7) also reported that SR-induced oxidative stress to hair proteins is exacerbated by trace elements and air pollutants that catalyse oxidative reactions and generate ROS [30,31,43]. Hence,

lifestyle factors have the potential to cause oxidative hair damage in locations with less intensive SR.

### 3.2. *Protein photodegradation*

Tryptophan degradation commonly serves as a marker for assessing protein photodamage due to its indole ring structure's UV absorbance properties [15–17,26,28]. Tryptophan degradation was evidenced by the increased presence of the two main tryptophan photodegradation products in the hair N-formylkynurenine and kynurenine, which are photosensitisers and could continue to perpetuate the process of protein degradation [14,26]. The resulting protein loss was then associated with the loss of structural integrity of hair, evidenced by increased swelling in water, interpreted as decreased protein cross-linking, and mechanical weakening, determined by Young's Modulus and stress-to-break values.

Other oxidative pathways in the fibre will be further discussed in Section 3.3. and 3.4. reporting the role of airborne pollution and trace metals, respectively.

A loss of cysteine-rich matrix protein S100A3 was reported in several studies [19,36,38] with some authors suggesting that the UV-induced loss of S100A3 may be attributable to cleavage of disulfide bonds. Other investigators examined the cumulative effects of heat styling treatments and UV radiation [44,45] on hair fibres and reported similar results. Fourier Transform Infra-Red (FTIR) spectroscopy and Near Infra-Red Spectroscopy (NIR) were also applied for measuring the degree of protein confirmation changes and cysteic acid accumulation following oxidative disulfide bond breakage [28,46]. Protein carbonylation is another marker reported in relation to oxidative damage [38].

All the studies, bar one, were conducted in laboratory conditions, subjecting hair of various colours (but all straight hair types) to different wave bands, intensity and length of SR equivalent. One atypical study involved hair tresses being exposed to daylight in Brazil [26]. Its alignment with the other *ex vivo* laboratory studies suggests that simulated solar exposure under experimental laboratory conditions could capture key aspects of solar-induced damage.

### 3.3. *Melanin degradation*

Although less researched within the selected reviewed articles, hair melanin has also been reported to degrade following exposure across the UV-visible-IR spectrum. Where varieties of hair colours were irradiated and colour changes compared via spectrophotometry, significant loss of colour and/ photo yellowing was reported in white hair [15,45]. Some authors suggested that visible and UVA light bands altered the structure of the melanin granules, whilst the UV light attacks protein structures preferentially [14,23]. Exposure to UV radiation, and solar radiation more broadly, was also found to affect hair melanin directly, with more significant changes attributed to the ability of longer wavelengths to reach the cortex [18]. This was particularly evident in lighter, blond or bleached hair which exhibited greater susceptibility to UV radiation damage [8,11,35]. This is likely due to the decreased melanin content of the hair, in particular, lower levels of eumelanin [22,23]. However, visible light was found most responsible for changing the natural colour [23] whilst IR radiation has been linked to the yellowing of natural white hair [15]. Eumelanin was suggested to withstand prolonged UV exposure and to provide some protein protective function [16,22,45,47]. The variations in hair colour and lack of detail in exposure protocols

across these studies make direct comparisons challenging, but allude to one common factor: that the degree of hair pigmentation is a key determinant of melanin photodamage.

#### 3.4. *Lipid oxidation*

Lipids are the main component of the CMC. As the CMC sits on the outermost outer layer of the cuticle cells, the loss of 18-MEA because of extensive UV exposure was found to be comparable with that of repeated bleaching, which causes hydrolysis of the thioester bonds in CMC [24,36]. At both fibre and tress levels, the loss of 18-MEA following UV radiation was reported to cause increased hair hydrophilicity and wet combing force [17].

The effects of UV radiation on lipids in hair from three different origins (African, Asian and Caucasian) were explored via structural image analysis, showing lifted edges (SEM) and bulging and disruption in the lipid layers (TEM) [27]. Similar damage to the CMC was observed after UV irradiation of wet hair, with hydroxyl radicals' detection, resulting in the formation of peroxidised lipids [29]. Other analyses of exposed hair came to the same conclusion: that UV exposure causes extensive lipid damage in hair [33][35][37].

In summary, this range of variable biomarkers and whole fibre and tress measurements evidence the extensive deleterious effects of solar radiation on hair protein and lipids. These studies confirm and expand on the various mechanisms of hair degradation and related morphological changes, first described in detail in two seminal book texts [4,48].

#### 3.5. *The effects of pollution*

Airborne pollution is defined as contamination of outdoor and indoor environments by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere [49]. According to the World Health Organisation (WHO) more than 99% of the world's population live in areas where the air pollution is above WHO air quality guidelines [49]. The main outdoor air pollutants derive from gaseous compounds such as Polycyclic Aromatic Hydrocarbons (PAHs), particulate matter (PM) and heavy metals [50,51].

However, as pollution levels in many large cities continue to rise [52–55], the research into the effects of pollution, both air and water borne, on hair becomes more relevant, including the combined effects of SR and pollutants. To date, one systematic review has reported that PM causes oxidative stress and damage to hair, together with scalp problems and follicular inflammation [56]. However, the authors did not consider the remaining hair exposome factors.

### 3.6. Airborne Particulate Matter

Studies of the pollution effect on hair have taken various approaches to mimic exposure. Notably, *ex vivo* laboratory pollution simulations lack the SR factor, whilst atmospheric pollution and solar radiation are intrinsically interconnected under real-world conditions. Hence, *in situ* exposure to airborne particle pollution and solar radiation appeared to be a preferred methodology, with morphological changes to the hair surface commonly reported, including cuticle delamination and lifting, increased contact angle, increased combing force and decreased shine [43,57–60]. These studies highlight a focus on consumer discernible fibre characteristics. Biomarkers of oxidative damage were also reported in some cases, with an increase of cysteic acid and protein carboxylation being associated with increased presence of PAHs in the air [42,57,61]. The

outcomes of these studies suggest cumulative impact and synergistic actions [12]. High airborne PM pollution was reported to affect the hair fibre surface by increasing surface friction, combing force and decreasing shine [37]. However, all studies lack control data, which would definitively distinguish true synergistic effects from confounding or additive damage.

In summary, multiple factors can influence the acceleration of SR damage on hair, and controlling and protecting against these environmental elements could enhance hair appearance and longevity [34]. Future studies should explore these factors collectively, as some have done, to depict the exposure consumers may experience more accurately. The hair status, too, has an impact, with naturally lighter and chemically bleached hair being most susceptible [35, 49, 52] and, therefore, requiring better-designed research protocols for a wide variety of hair types, colours and textures.

### 3.7. *Water borne contaminants*

Water borne contaminants such as trace metals, including iron, copper, lead, zinc and magnesium, are common in groundwater due to industrial activities and old pipework, but their concentration is normally controlled to levels below those causing harm to human health. Hair may be exposed to trace metals daily, via the water, and particularly, dissolved copper ions are ubiquitous in pipes. Their presence in hair has been reported to cause free radical formation, which is enhanced under UV radiation and wet conditions [30,31,34]. Furthermore, copper exposure was associated with increased protein loss and lipid peroxidation, indicating accelerated damage [30]. In summary, copper, which is ubiquitous in water, has emerged as the most significant factor leading to exacerbated protein damage in hair.

Other trace metals such as calcium, iron, cadmium and lead have also been found to be present in the hair, assumed to be due to air pollution and/or the quality of the water used for washing and are known to cause protein degradation [62–64].

### 3.8. *Examples of damage prevention approaches*

Whilst the impact of the above elements of the hair exposome (SR and pollution) is well evidenced, the exact mechanisms and therefore possible mitigation of these effects are less clearly presented in the literature. However, skin-protection approaches such as filtering UV radiation and the use of antioxidant actives have been trialled with studies reporting colour, shine and mechanical preservation following the application of shampoos or leave-on cosmetic products to hair before irradiation with UV light [9,10, 14, 22, 25, 29, 31,32]. Selective chelators of copper and other trace metals in water have also been tested [27, 56].

## 4. **Methodological summary**

Scoping the methods for measuring the oxidative hair damage was one of the aims of the review process. The earlier investigative studies commonly relied on reporting the direct photodamage by measuring and comparing tryptophan levels via fluorescence spectroscopy, and the detection of its degradation byproducts via chromatography-MS. However, these methods do not detect the whole range of oxidative reactions taking place in the hair, such as the disulfide bond and thioester bond cleavage in the presence of ROS, leading to protein and CMC structural alterations. Hence, methods such Electron Paramagnetic Resonance (EPR) have been used more recently for detecting free radicals *in situ*, whilst

FTIR is more commonly used to infer the lipid oxidation. SEM and TEM are commonly used for illustration of the macro structural fibre damage, such as cuticle delamination, and chipping and voids within the hair cortex, presumably resulting from the gradual removal of protein and lipid fragments generated as a result of oxidative reactions. Studies that incorporated several of the above techniques were more successful in reporting the oxidative damage at the molecular and structural levels. Consumer-relevant tests such as combability and shine were included in some studies; however, the inclusion criteria for study selection in this review aimed to scope the more fundamental fibre knowledge, hence fewer studies included hair assembly investigations. A full list of the various methods for hair fibre and assembly analysis is available in *Supplementary Table 2*. Furthermore, to enable comparability of the published literature, studies should, at a minimum, report the irradiance ( $\text{Wm}^{-2}$ ) and exposure time, from which the cumulative radiant dose could be derived for more precise comparisons. Alongside the spectral range, these values define the total energy delivered and its biological relevance.

## Conclusions and future directions

Despite the differences in tested hair and biochemical data points, the potential for SR and pollution to cause damage to human hair in some contexts was clearly evidenced. Across all 40 studies reviewed, the damaging effects of SR, airborne pollution and trace metals were observed at molecular protein and lipid levels and in the hair's morphological structures. The extend of these effects were demonstrated to depend on the natural hair colour (quantity and type of melanin) and the pre-existing hair damage due to cosmetic treatments. Collectively, the studies confirm that bleached, permed or heat-treated hair,

lighter coloured or non-pigmented hair incur higher degree of damage which represents an opportunity for more targeted protection solutions.

The SR studies concluded that SR penetrates the human hair and the key factors affecting the level of damage, besides the hair status, are the wavelengths, intensity and the irradiance, thus geographical location is a key risk factor. The synergistic oxidative effect with airborne pollution, highlights the further increased risks in locations where prolonged SR exposure is combined with high urban pollution. Trace metals in the water exacerbate these effects, presenting a case for continual oxidative stress management for some hair types.

In summary, the research suggests a multifactorial effect of hair characteristics and environmental factors on the oxidative stress incurred by the hair fibre in its life span. Hence a unified hair exposome model, analogous to the exposome approaches adopted in skin research over the past decade, can be developed. A unique element of human hair interaction with this exposome is that the scalp and the hair follicle are also subjected to it, despite the hair's very specific evolutionary role to protect the scalp. Moreover, applying treatments would also be commonly done in a manner that covers both hair and scalp. Hence, combined protection strategies could be considered. Hair exposome framework is also well suited to future extension of research into scalp health and hair growth support, which are also of significance to the single fibre and the head of hair health and appearance.

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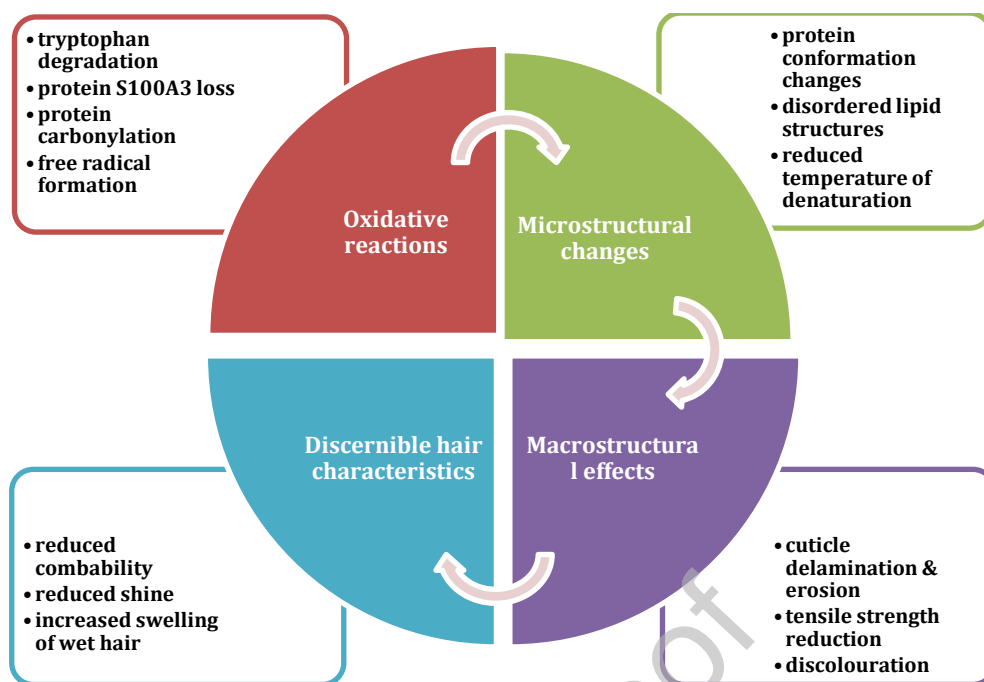
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## Graphical abstract



Manifestations of hair damage resulting from the combined exposure to solar radiation, pollution and trace metals.

#### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: