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Radon as an anthropogenic indoor air pollutant as exemplified by radium-dial watches and other uranium- and radium- containing artefacts.

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Abbreviated Title: Radon an Anthropogenic Indoor Pollutant

Abstract.

Radon is generally regarded as a naturally occurring radiological hazard but we report here measurements of significant, hazardous radon concentrations that arise from man-made sources, e.g. radium-dial watches. This study is an examination and assessment of health risks from radium and uranium found in historical artefacts, and the radon that emanates from them. This includes radium-dial watches, the main focus, plus clocks, aircraft instruments, and ornaments and artefacts made of uranium glass / uranium-glazed. Such objects were very popular in the 1930s and 1940s and are still readily available today.

A collection of 30 radium-dial pocket and wrist watches was measured and shown to be capable of giving rise to radon concentrations two orders of magnitude greater than the UK Domestic Action Level of 200 $Bq \bullet m^{-3}$ in unventilated or poorly ventilated rooms. Furthermore, individual watches are capable of giving rise to radon concentrations in excess of the UK Domestic Action Level. We also highlight a gap in remediation protocols, which are focused on preventing radon entering buildings from outside, with regard to internally-generated radon hazards. Radon as arising from man-made objects such as radium-dial watches should be considered appropriately in radon protocols and guidelines.

Key words: Radium, radon, watches, clocks, aircraft dials, uranium glass, uranium ceramics, health hazards.

Introduction.

Radon is generally regarded as a naturally occurring radiological hazard but can also arise from man-made materials, e.g. building materials, ornaments (and fittings) and collectible items. Of these, building materials have received reasonable attention but ornaments and collectibles have been largely overlooked in terms of exposure and dose to the general population and remediation of buildings.

As we note in our companion paper (Gillmore, Crockett, Phillips; this volume), the emphasis on radon remediation is, rightly, the paired objectives of preventing radon ingress into buildings and minimising any accumulation of radon in buildings.

Radon occurs as three isotopes, ^{222}Rn (hereinafter 'radon'), ^{220}Rn ('thoron') and ^{219}Rn ('actinon'). Radon (^{222}Rn) is part of the uranium, ^{238}U, decay chain and is the direct decay product of radium, ^{226}Ra, and is considered to be the main radiological health hazard to the general population owing to its half-life of 3.82 days which allows it to accumulate in the built environment. Thoron (^{220}Rn) is part of the thorium, ^{232}Th, decay chain and is the direct decay product of radium, ^{224}Ra, and has a half-life of 55.6 s. Actinon (^{219}Rn) is part of the uranium, ^{235}U, decay chain and is the decay product of actinium, ^{227}Ac, via ^{220}Th and ^{223}Ra, and has a half-life of 3.96 s. Neither of these short-half-life radon isotopes are generally considered to be radiological health hazards to the general population owing to their short half-lives which significantly limit their accumulation in the built environment. The ^{238}U and ^{232}Th decay chains are shown in Figure 1 (published with permission from the World Nuclear Association).

<u>Building Materials.</u>

The main radiological hazard generally considered in the context of building materials is that which arises from gamma radiation. Many building materials contain small amounts of radioactive elements, mainly radionuclides from the ^{232}Th and ^{238}U decay chains, which give rise to radon isotopes, ^{220}Rn and ^{222}Rn respectively, of which ^{222}Rn is the main radon hazard due to its potential for accumulation.

In general, the radioactive content of building materials reflects the radioactive content of the raw materials from which they are made (Mahur et al., 2008; Righi and Bruzzi, 2006; Amin, 2015; Keller et al., 2001; Khan, 1994; Petropoulos et al., 2001 & 2002, Stoulos et al., 2003; Chen et al., 1993 & 2010; Zhang et al., 2012). In the case of building stone, such as granites and ironstones, the content of the building materials is exactly as quarried. In the case of bricks and blocks, radioactive materials may be diluted by the addition of other materials. The increasing use of industrial by-products in building materials may add to exposure to radon (Amin, 2015; Keller et al., 2001).

In buildings made substantially of brick, concrete or stone, those materials attenuate the indoor levels of radiation emitted outdoors but can be the main source of exposure and dose indoors (Righi and Bruzzi, 2006). The amount of radon released into the internal (and external) environments depends on the structure and surface properties of the particular materials (Keller et al., 2001): materials with relatively open structures and surfaces in general allow higher rates of radon emanation than those with relatively closed structures and surfaces.

Gypsum (phosphogypsum), which is a by-product of the production of fertilisers, is widely used in the production of building materials, including decorative internal materials (Maged and Ashraf, 2005). This waste gypsum contains much of the radium originally in the phosphate rock from which it was derived and, as well as the building materials which incorporate it, the piles of waste gypsum are a source of radon emission to the environment. Ash and slag from coal-fired electricity generation stations is used in the production of cement and other building materials such as blocks and bricks (Keller et al., 2001, Petropoulos et al., 2001 & 2002).

Uranium and Thorium Glass Objects and Glazes

According to Lopes et al. (2008) the earliest reference to uranium in glass appears to be in 1817 and uranium oxides have been used, together with uranates (e.g. potassium (di)uranate, $K_2U_2O_7$) for colouring glass and as a colouring agent in ceramics since the 19th Century. Initially, during the 19th Century, two colours were developed – yellow and green uranium glass (see Figure 2) – and, typically, such glass contains between 0.5% and 4% (maximum) by weight of uranium oxides. The colour intensity does not appear to increase with greater concentration of oxides (although the luminescence does) so most glass contains around 0.5% ^{238}U. The radioactivity emitted from glass objects tends to be mainly from ^{238}U and its daughters, ^{234}Th and ^{234}Pa (Lopes et al., 2008).

New controls on radioactive substances were introduced in the 1940s in the UK and the USA (see IAEA Report, 2004) and the US government banned uranium salts from commercial use due to their strategic potential during WWII. Since then the use of uranium in glass and glazes has been discontinued although depleted uranium has been used in more recent times. Measurement of radon exhalation from glass and glazed objects (see Figure 2) has been very limited with most authors concentrating on measuring other aspects of radioactivity (see Kierzek et al., 2000). Hansen and Moss (2015) examined a uranium glass necklace in terms of its potential health impact on the skin for its wearer, one of their original areas of interest in this study being any potential risk to the wearer from radon as the necklace would be worn near the mouth and nose (Hansen pers com.). Using pig skin as a human skin surrogate they found the potential health risk required further investigation, although they stated that beta particles from the radon progeny decay chain ^{218}Po and ^{214}Po, were particles of particular concern, plating out onto the skin. Their measurements involved using solid-state nuclear track detectors (SSNTDs) next to the necklace and the skin.

Uranium (and thorium) glazes were used for floor tiles, pottery and other ceramics and in cloisonné jewellery. In the USA Fiesta commenced production of coloured dinnerware in 1936, and most coloured ceramics with uranium based glazes were produced before WWII although production didn't cease until 1944. The most radioactive of these appears to be a popular red glaze and, after WWII use of this this glaze was continued, using depleted uranium in place of ^{238}U, through to the 1970s. Glazes such as these were estimated by Piesch et al. (1986) to be 0.2 mm thick. Buckley et al. (1980) suggested that a single Fiesta-ware plate contained 4.5 grams of uranium. Paul Frame (2015) from the Oak Ridge Associated Universities in the USA suggests that by weight, up to 14% of the glaze in Fiesta ware may be uranium.

Zeman and Hon (1994) suggest that radon emanation from products such as Fiesta-ware would contribute to indoor radon concentrations, in the order of 1,000 $Bq \cdot m^{-3}$ in an unventilated room. However, there is also a suggestion that uranium glaze would not be a source for radon because it contains chemically purified uranium and not the complete uranium decay series (Kitto et al., 1996). In other words, the glaze would contain ^{238}U (plus small amounts of the first decay products ^{234}Th, ^{234m}Pa, ^{234}Pa, ^{234}U), ^{235}U and ^{230}Th (and its decay product ^{231}Th) but assumes that there is insufficient time either for any ^{226}Ra to have arisen between purification and the time of manufacture or for any ^{226}Ra to arise subsequently via the decay processes. This implies that no radon would be generated except by the body of the ceramic (Frame, 2015). However, Kitto et al. (1996) highlight that the ^{232}Th decay series had established equilibrium in the glazes they examined, although in low concentration which may have prevented their detection of radon (thoron).

However, where there is consensus regarding glazes is the concern over exposure to gamma radiation. Buckley et al. (1980) suggest that exposure rates of 5 to 150 $\mu Sv \cdot h^{-1}$ at the surface of a plate and 0.02 to 3 $\mu Sv \cdot h^{-1}$ at 1m was not unreasonable. Another exposure pathway was to the hands from beta particles. Piesch et al. (1986) suggests that 320 $\mu Sv \cdot h^{-1}$ was possible at the surface of a red Fiesta-ware teacup whilst Frame (2015) suggested that such a teacup would give a person an effective annual radiation dose of 4 mSv to the lips and 12 mSv to the fingers if used daily. Lastly there is a risk of ingestion of uranium leached into food (see Landa and Councell, 1992). For example, after immersing red glazed ceramics in a 4% acetic acid solution for 24 h, the concentration of uranium in the leachate was 3.1 $mg \cdot L^{-1}$ (Landa and Councell, 1992).

Ceramic items such as a Revigator Dispenser were used to generate radon enriched water. The glazed ceramic body of the jar had a porous lining that incorporated uranium ore (see Epstein et al., 2009). Such curios have been found to still give of an appreciable amount of atmospheric radon.

Radium Dials

Radon is generally regarded as a naturally occurring radiological hazard but, in our previous paper (Gillmore et al., 2012), we investigated the general radiological hazards arising from radium-dial watches, as a specific type of collectible artefact (Figure 2). Those hazards include radon, which arises from the radium in the watches, i.e. an anthropogenic source of radon. Our previous research built on earlier research by the National Council on Radiation Protection and Measurements in the USA (NCRP, 1977) and Boerner and Buchholz (2007) on radiation exposure from consumer products. Those earlier investigations noted radiation exposures and doses arising from radioluminescent paints, particularly as used on watch and clock dials (see Figure 2). Those paints consist of radium (^{226}Ra, half-life of 1600 years), mesothorium (^{228}Ra, half-life of 5.8 years) and radiothorium (^{228}Th, half-life of 1.9 years) in the form of insoluble sulphates in a matrix of crystalline phosphorescent (i.e. doped) zinc sulfide (ZnS) (Martland and Humphries, 1973). The doping was generally copper, which results in the archetypal blue-green luminescence, and which has the additional advantages of being stimulated by ultra-violet light and having a long-duration fade to darkness, but other metals were also used to dope the zinc sulfide, including manganese (with copper) which resulted in an orange luminescence.

Production of radium-based luminescent aircraft instrumentation began in the 1920s, utilising hand applied paints, the decay chain of which emits alpha and beta particles together with gamma radiation. At the time of production the impacts of radium on human health were not fully appreciated. However, as a result of studies such as those on radium watch dial painters in the USA significant health issues were identified, e.g. necrosis of the mandible and maxilla, bone tumours and jaw-bone porosity (BEIR IV, 1988; Evans, 1966; Stehney, 1995). We now understand much more about the impact of ^{226}Ra ingestion on human health (see Gillmore et al., 2012).

The maximum travel distance of an alpha particle in air at Standard Temperature and Pressure is under 10 cm, for beta particles it is an order of magnitude greater. A layer of dead skin can act as a barrier to alpha particles although such particles can have a significant biological effect if inhaled, ingested or injected, i.e. if introduced into the body. Highly ionising alpha particles can interact strongly with matter and come to a sudden halt due to a rapid loss of energy – which is why such radiation has a radiation weighting factor (WR) of 20 (see the European Commission Proposal for a Council Directive COM(2012) 242 final 2012-05-30).

During our previous investigation (Gillmore et al., 2012), we observed that as well as the hazard arising directly from the radium and thorium isotopes, there was also a significant hazard arising from radon (^{222}Rn). However, at that time, we were only able to undertake preliminary investigation of the radon hazard owing to the high radon concentrations arising from the collection of watches (Gillmore et al., 2012). In this paper, we extend our consideration of the radiological hazards arising from radium-dial watches with a more detailed investigation of the hazard arising

from the radon that emanates from them and causing significant increases in the radon concentrations in the surrounding air. A more comprehensive investigation of potential radon hazard arising from uranium sources is underway but some very preliminary comments are presented here.

Watches – Method.

The preliminary investigation of the radiological hazard arising from radium-dial watches (Gillmore et al., 2012) indicated significantly higher than expected radon concentrations arising from the collection of watches. In that investigation, the container used to house the collection of watches was placed in a ventilated laboratory of volume 67.3 m^3 and concentrations reaching 2-3 $kBq \bullet m^{-3}$ were observed in the laboratory, in the vicinity of the container, when the building ventilation system was not in operation. Such concentrations are an order of magnitude higher than the UK Action Levels (200 $Bq \bullet m^{-3}$, domestic; 400 $Bq \bullet m^{-3}$, workplace) and so the investigation was suspended pending development of a new experimental method which would not necessitate restricting access to the laboratory due to potentially hazardous radon levels (here we use 'hazardous' to mean exceeding the workplace Action Level).

The aim of the investigation we report here was to gauge the order of radon concentration and, hence, radon hazard, that can arise from a collection of radium-dial watches as might be kept in a private dwelling by a private collector. This investigation follows the same basic principle as the preliminary investigation which is to place the watch or watches in a known volume of air and monitor (hourly sample) the increase in radon concentration as it rises towards equilibrium. The exponential rate constant and equilibrium radon activity can then be obtained from the resultant time-series of radon concentrations and, from there the overall radon activity and effective radium content for the collection as a whole can be calculated. Ideally, that known volume of air would be on the same order as that of, say, a typical small bedroom or study as might be used by a collector to house their collection but this was not possible due to the high levels of radioactivity associated with the watches, as reported previously (Gillmore et al., 2012). However, we use the radon concentration measured in a controlled experimental volume of air to estimate radon concentrations for a hypothetical room of the same size as the study of one of the authors, that being 2.44 m wide by 2.74 m long by 2.44 m high, volume 16.3 m^3. That is not the room used to house this particular collection of watches, this being housed in a radiation-proof ventilated room at Kingston University.

It should be noted at this point that some of the watches in the collection are relatively fragile, e.g. with luminescent paint that has degenerated over time and crumbled to dust inside the watch casing, and/or with decayed seals and damaged glasses. Therefore, for this and radiological safety reasons, we endeavoured to keep handling of the watches, particularly the fragile ones, to a minimum so as minimise the potential for further damage, including potential loss of radioactive

material. This necessitated measuring the majority of the watches 'as housed' and 'as mounted', i.e. measuring the collection as a whole or in subsets rather than as individual watches. As the primary aim of the investigation was to investigate radon concentrations which arise from the collection as a whole, this was not a significant constraint but it did restrict measurement of individual watches to six which were in good, usable, physically wearable, condition.

In light of the high levels of radon emanation known to occur for at least some of the watches, it was necessary to conduct the measurements using a closed-loop arrangement in a ventilated fume cupboard in a laboratory. The measurements were made in two phases and both phases used the same basic experimental arrangement. This consisted of a (sealed) container, in which the watch or watches were placed, connected to a (sealed) column of drying agent and a Durridge RAD7 in a closed loop. This is shown schematically in Figure 3 and, with the exception of residual small leaks in the RAD7, drying column, etc. both variants were sealed systems, i.e. controlled experimental volumes. The first phase had two objectives: it was in part measurement of individual watches and also in part a scoping exercise for the second phase. In the first phase, individual watches were placed in a small-volume container of volume 7.0 L, giving a total loop volume of 8.7 L. On the basis of these measurements, a polypropylene barrel of volume 127.5 L, the biggest container which would fit safely inside the ventilated fume cupboards in the laboratory, was used for the second set of measurements, giving a loop volume of 129.2 L. Even with a container of this volume, the collection of watches had to be measured in two subsets because with the whole collection at once, the radon concentration in barrel rose above the RAD7's calibrated maximum level of 750 $kBq \bullet m^{-3}$ (Durridge, 2015) before sufficient data could be logged to derive the equilibrium and radium-radon activity.

Watches – Results.

In total, six individual watches were measured, using the 7.0 L container, and the whole collection was measured in two subsets, using the 127.5 L container.

The individual watch measurements generally yielded 'noisier' data than the subset (multiple watch) measurements: in the subsets, individual variations are effectively smoothed by the aggregation with the other watches in that subset. In general, the recorded hourly sampled data corresponded closely to expected exponential increase towards a steady-state equilibrium concentration. Overall, there are two main features of the measurement process which affect the rate at which the radon concentration in the closed system increases towards equilibrium. These are (a) plating out of radon and daughter nuclides onto internal surfaces and (b) changes in radon emission rates from watches due to changes in the properties of non-radioactive watch materials and components (e.g. seals and gaskets) as a consequence of the dehumidification of the air in

the closed loop. In general, these processes are gradual with time, effectively resulting in gradual changes in the exponential rate constant as the time increases.

In addition, short-term fluctuations in the radon concentration were observed. These were of two general types and both were proportionally smaller during the earlier part of the measurement period when the radon concentration increased rapidly and, conversely, proportionally bigger, more apparent during the later part of the measurement period when the radon concentration levelled out towards equilibrium. First, quasi-periodic variations which show weak correlation ($R \lesssim 0.5$) with temperature, with variations in radon concentration lagging changes in temperature by ca. 15 hours. Second, apparently random small changes in the radon concentrations which are tentatively attributed to changes in material properties of the watch, as the air in the closed loop is dehumidified, changing the rate at which radon emanates from the watch. A typical accumulation of radon with time is shown in Figure 4, for the Helvetia wrist watch.

As a consequence of these observations, a 144 hour time window, from 7 hours to 150 hours, was identified as a consistent time-window for all the measurements which (a) allowed time for the system to settle at the beginning and (b) ended before changes in the rate constant became observable, i.e. comparable to the hourly change in radon concentration, and (c) corresponded to the period of maximum rate of change of radon concentration.

For the 144 hour time window, the recorded hourly sampled data corresponded closely to the expected exponential increase towards a steady-state equilibrium concentration as given by

$$Rn(t) = Rn_{eq}(1 - e^{-k(t-t_0)}) \qquad (1)$$

where

$Rn(t)$ is the radon concentration at time t,

Rn_{eq} is the steady-state equilibrium concentration,

k is the total rate constant, $k = k_{Rn} + k_{leak}$,

k_{Rn} is the radon radioactive decay constant,

k_{leak} is the leakage rate constant,

t_0 is an initial time offset from zero to allow for any time difference between sealing the system and starting the RAD7.

The modelled exponential increase for the Helvetia wrist watch is also shown in Figure 4 with pictures in Figure 2.

It is clear from Figure 4 that the modelled exponential increase is a good fit to the initial part of the data where the rate of increase is greatest but that as the rate of increase slows, i.e. towards 200 hours, the radon concentration shows variations from the exponential. The quasi-periodic variations observed for some watches are not visible for this watch but there are small steps in the

measured radon concentration at ca. 160 and 190 hours, attributed to changes in the rate at which radon emanates from the watch due to changes in material properties of the watch.

The zero-leakage equilibrium concentration can be calculated using the relationship

$$Q = k_1 Rn_{eq,1} = k_0 Rn_{eq,0} \quad (2)$$

where

Q is the (constant) rate of radon emanation from the watch(es) due to the decay of the radium in the paint, i.e. the influx into the measuring system,

$Rn_{eq,1}$ and k_1 are the steady-state equilibrium concentration and rate constant with leakage,

$Rn_{eq,0}$ and k_0 are the steady-state equilibrium concentration and rate constant without leakage.

This yields the relationship

$$Rn_{eq,0} = \frac{k_1}{k_0} Rn_{eq,1} \ , \quad (3)$$

and from there, knowing the volume in which the activity concentration was measured, the effective activity actually emanating from the watch(es) can be calculated. At equilibrium, the decay rate is equal to the radon influx, i.e. the effective radon activity emanating from the radium decay, and is thus a measure of the effective radium content of the watch(es).

In order to calculate equilibrium concentrations and rate constants, the measured radon concentrations were non-linearly regressed against time for the 144-hour period, 7-150 h, to (a) minimise initial dis-equilibration effects and (b) ensure as far as was possible that conditions were consistent across all measurements and include the period of maximum rate-of-increase of radon concentration to optimise the non-linear least-squares fitting algorithm in R in fitting the data (https://www.r-project.org).

The effective radon activity and equilibrium data are shown in Table 1. In addition to the calculation of zero-leakage equilibrium concentration and activity, the concentration that would arise in a hypothetical unventilated room of dimensions 2.44 m wide by 2.74 m long by 2.44 m high, volume 16.3 m^3, representative of small bedroom or study as might be used by a collector to house his/her collection. It is clear from these calculations that as well as the whole collection giving rise to a hazardous radon concentration of 13.24 kBq•m^{-3} approximately 67 times the Domestic Action Level of 200 Bq•m^{-3}, three of the watches individually (the Cyma pocket watch, the Moeris wrist watch and one of the Newmark wrist watches) would give rise to a hazardous radon concentration in excess of 200 Bq•m^{-3}.

The inferred radium content and the effective radium content calculated from the effective radon activity are shown in Table 2. The inferred radium content was calculated as described in Gillmore

et al. (2012). In brief, a Thermo Electron Mini Rad 1000 (http://rp-alba.com/index.php) was used to measure gamma dose rates 2 cm from the watch faces and these measurements were compared to the ambient equivalent gamma dose rates from three nominal 185 kBq (5 µCi) Panax ^{226}Ra sources. This type of source comprises an active component (a radioactive foil) in a cup-type holder with an outer wire mesh (e.g. see Figures 1, 2 in Whitcher, 2009).

There is clearly much variation in the ratio of effective to inferred radium content, as expected from the variation in materials, constructions and conditions of the watches. The most hazardous watch measured is the Cyma pocket watch, where almost all (99.5%) of the inferred radium content gives rise to radon which escapes from the watch. At the other extreme, for the Moeris wrist watch, only 13.8% of the inferred radium content gives rise to radon which escapes from the watch. Overall, across the whole collection, 56.0% of the inferred radium content gives rise to radon which escapes from the watches.

However, the collection overall represents a significant radon hazard, indicating an equilibrium concentration in the hypothetical room ca. 67 times the UK domestic Action Level, with three individual watches indicating equilibrium concentration in this hypothetical room above the UK domestic Action Level.

Other Anthropogenic Radon Sources – Methods.

As well as the investigation of the radium dials, it is our intention to investigate other collectible and ornamental items, including a WWII altimeter, various uranium glass ornaments and uranium-glazed ceramics, and building / decorative stone samples. Some of these have been investigated on a preliminary scoping basis, with a fuller investigation to follow.

A Thermo-Scientific RadEye B20 Multi-Purpose Survey Meter and a MINI 900 series Type 44b Scintillation Monitor (http://www.thermoscientific.com/en/home.html) were used to take initial scoping measurements of the radioactivity emanating from: an altimeter, purporting to be from a WWII Spitfire; two bedside clocks; a Fiesta-ware red glazed teapot and lid; a 23 cm circumference green glass dish; a polished UK-granite door-stop (2.79 kg); and fragments of uranium-glazed ceramic and yellow uranium glass.

With regard to radon, the altimeter, granite door-stop and uranium glass dish were monitored in the closed-loop configuration, with the 127.5 L container, as used for the watches, in order to obtain a provisional estimate of their radon activities. Also, the teapot and lid were scoped for radon activity using the closed-loop configuration with the 7.0 L chamber, and the teapot was tested with SSNTDs using the 7.0 L chamber.

Other Anthropogenic Radon Sources – Results.

The altimeter, teapot and dish are shown in Figure 2. The preliminary results are shown in Table 3 and the provisional radon activity results are shown in Table 4. The radon activty results for the altimeter and granite door-stop are robust but those for the uranium glass dish, teapot and lid should be regarded as indicative owing to the small, close-to-background, radon concentrations being measured.

The teapot lid yielded a radon concentration of ca. 43.5 Bq•m^{-3} in the small closed-loop system, i.e. a radon activity of ca. 610 mBq, and the SSTND measurements yielded an unadjusted mean concentration of 113 Bq•m^{-3} over a 19-day period, corresponding to a total alpha activity of 791 mBq. The total alpha activity is approximately 30% greater than the radon activity indicating that there are other alpha emitters present, e.g. radon (^{222}Rn) daughters ^{218}Po and ^{214}Po (and possibly thoron (^{220}Rn) and daughters ^{216}Po, ^{212}Po and ^{212}Bi), noting that the equlibrium factors in the SSNTD calibration have not been adjusted to account for the specific equilibrium conditions in the measurement system. The teapot yielded a radon concentration of ca. 73.4 Bq•m^{-3} in the small closed-loop, i.e. a radon activity of ca. 860 mBq, approximately 40% greater than that of the lid and attributed in part to its greater surface area.

In effect, the teapot and lid and glass dish do not produce radon concentrations significantly higher than the background which, in the ventilated laboratory, was typically ca. 2 Bq•m^{-3}, and so these items are unlikely to be hazardous sources of radon unless kept in small confined spaces. However, the results for the altimeter are comparable to those of the watches, indicating radon activity equivalent to several watches, and indicate an equilibrium concentration in the hypothetical room ca. 33 times the UK domestic Action Level – a significant hazard. This should not be surprising noting the size of the dial and the multiple luminous scales. Also, the results for the granite door-stop indicate an effective radon emanation of 19.7 Bq•kg^{-1}, but the indicated equilibrium concentration in the hypothetical room is only ca. 1.7% of the UK domestic Action Level – so of itself is unlikely to present a significant hazard. However, the granite door-stop is only very lightly fractured, polished and possibly surface-treated, implying the total bulk emanation could be significantly higher than the effective radon emanation of 19.7 Bq•kg^{-1}. We calculated a bulk emanation of 165 Bq•kg^{-1}, for the door-stop, indicating that radon concentrations arising from either granite objects with higher surface-area to volume ratios or objects made from less polished and more fractured granite could potentially be an order of magnitude higher (although still only on the order of 15-20% of the UK domestic Action Level for an object of similar mass to the door-stop).

Anthropogenic Thoron Sources.

Many of these items, including the watches, altimeter, granite block and uranium glass – but not the glazed teapot or lid – also indicated significant thoron emanation. These preliminary measurements were made using the RAD7 ‘thoron mode’ during the radon closed-loop measurements described above. Preliminary thoron data are presented in Table 5.

Thoron occurs as part of the thorium decay chain, which also includes mesothorium (^{228}Ra) and radiothorium (^{228}Th), and so is to be expected as a radioactive emanation from (a) watches containing paints containing mesothorium and/or radiothorium and (b) monazite granites containing thorium but our results indicate that some uranium glass also contains elements from the ^{232}Th decay chain as impurities.

In general, thoron accumulation in the built environment from external sources is not considered to be a problem owing to the short half-life, which severely restricts thoron migration into and accumulation in buildings. However, our preliminary measurements indicate that significant accumulations could potentially arise from internal sources and, in relatively still indoor air whilst the short half-life will still act to restrict accumulation, there will be significant thoron concentrations around any such internal sources.

Discussion.

Although the measurement of individual watches was limited to six, one pocket watch and five wrist watches, owing to their general physical condition and fragility, measurement of the collection as a whole was possible, albeit in two subsets to keep the radon concentration within the RAD7's calibrated range during the initial 150-hour period. This enabled us to demonstrate that the radon emanating from radium-dial watches is significant and can easily constitute a health hazard if a collection of watches is kept in an unventilated or poorly ventilated room. Also, whilst our results show directly that this collection of radium-dial watches would raise the radon concentration to hazardous levels in an unventilated or poorly ventilated small room (the final row in Table 1), it is clear that this collection is capable of raising the radon concentration to hazardous levels in significantly greater volumes, e.g. hypothetically, volumes of whole houses. Thus, rooms used to store collections should be actively ventilated to the external environment to prevent or inhibit the diffusion of radon to the rest of the house.

In addition to collections of watches posing a potential health hazard, these results show that radon emanations from individual watches can pose a health hazard: three of the individual watches measured had the capability to raise radon concentrations above the UK Domestic Action Level of 200 Bq•m^{-3} in unventilated or poorly ventilated rooms. This is of concern because it is known anecdotally that in addition to military watches being particularly prized by collectors (see Wesolowski, 2006), many individual radium-dial watches are kept as mementoes of military service by ex-servicemen and their descendants. Whilst such persons might be aware that their watches are radioactive and so should not be worn (at least for any appreciable length of time), they are relatively unlikely to consider that a radioactive gas (radon) might be escaping from their watches, even if kept in 'shielded' containers, and have the potential to pose a significant health hazard to themselves and their families.

The other collectible items which we have investigated on a preliminary, scoping basis show that it is not just radium-dialled watches that are sources for indoor radioactivity. Whilst radium watch dials (and items such as bedside clocks) have been clearly shown to have the potential to generate significantly hazardous concentrations of radon in confined spaces, so can aircraft dials, perhaps not surprisingly noting their essential similarity to watch dials. Our initial investigation suggests that uranium glass may not be a significant source of radon in the home, although much more work needs to be done on this before we could make a more definitive statement. However radon progeny generating beta particles could be an issue for uranium glass jewellery and for crockery and glassware used for eating and drinking, i.e. items that come into physical contact or close physical proximity with the skin. Also, uranium glazes do generate some radon, as provisionally measured in a small sealed volume, indicating potential health hazards in small spaces. This is perhaps contrary to what some authors have suggested (Kitto et al., 1996). The concentrations generated though are not of the order suggested by Zeman and Hon (1994) in our preliminary study.

An interesting (relatively) recent development is that the IAEA Code of Conduct published in January 2004 contained a list of 16 radionuclides which are considered to be hazardous when present above certain quantity thresholds and which could be used for malevolent purposes. This list includes ^{226}Ra. As a result of this, the US Nuclear Regulatory Commission (NRC) was empowered through the Energy Policy Act in August 2005 to regulate ^{226}Ra which had not been the case prior to that date: prior to that date ^{226}Ra had been regulated by some US states but not at the Federal level. This only governs amounts of ^{226}Ra on the order of 37,000 MBq (1 Ci) or more, or significant collections kept, to be considered under this legislation. Controls exist in the form of a licensing process – a general or special license entitles individuals or organisations to hold certain materials, and watches with more than 37,000 Bq (1 μCi) of radium are liable for a license. Also, it is not permitted under certain circumstances to hold collections of a hundred items of radium containing materials / instruments (see http://www.nrc.gov/reading-rm/doc-collections/cfr/part031/part031-0012.html).

Whilst we have some understanding of the very large number of watches that were produced / in circulation with radium dials in the 1970s (some 10 million; NCRP, 1977; Gillmore et al., 2012), obtaining or making an estimate of the number of radium-dialled aircraft instruments made / in circulation is more problematic due to the nature of the (wartime) production and the classified nature of some military production documentation. Even more problematic is the estimation of the number of artefacts and ornaments made using uranium and thorium glass and glazes which are still in private dwellings, many of which were produced before any hazardous potential was appreciated. Furthermore, the amount of radiologically hazardous building material that has been used, noting that radioactive materials will have been naturally part of building stone and

incorporated into bricks, blocks, cements and concretes since mankind started building using stone and making building materials from sands and other geologically-sourced materials.

Whilst, in many respects, the radiological hazard presented by building materials has been quite well investigated, even though the actual amount of potentially hazardous materials is poorly quantified, there has in recent years been concern expressed over, in particular, decorative stone finishes such as granite worktops. Kitto et al. (2009) examined granite countertops and mantels using both continuous and integrating radon detectors. Each of their 24 samples emitted radon, which they measured using a similar technique to our controlled-volume system in placing granite cores in a sealed glass jar. Emanation from the granites examined gave results of up to 4 $Bq \bullet kg^{-1}$ using continuous radon monitoring, less than but comparable to our measurement of 19.7 $Bq \bullet kg^{-1}$, suggesting granite artefacts are relatively unlikely to present radon hazards unless, for example, they have high surface-area to volume ratios and/or are made from unpolished highly fractured granites and/or are situated in small, poorly ventilated spaces.

Lastly, it should also be remembered that thoron can contribute 50% or more to the potential alpha energy concentration (PAEC) in some dwellings according to Shang et al. (2005), with Zeeb and Shannoun (2009) noting that thoron generally originates from the walls of a building. Due to its short half-life in relation to the diffusion time, the concentration of thoron (from building materials in walls) will decrease towards the middle of a room. Similarly, thoron concentrations arising from an artefact, such as the altimeter or granite block described above, will decrease with increasing distance from that artefact. Thus, the hazard will be more localised than that from radon, due to shorter half-life and diffusion range, but potentially still significant if the artefact is in close proximity to the nose or mouth for extended periods, such as might arise if the artefact is being studied at close range for extended periods, e.g. through a (mineralogical) microscope or other optical magnifier, rather than viewed at a display distance.

Current guidance is primarily focused on the risks posed by radium and radium dust (see Evans, 1966; BEIR IV, 1988; Blaufox, 1988; HELA, 2001; HSE, 2002; Shaw et al., 2007). The UK Radioactive Substances (Clocks and Watches) (England and Wales) Regulations 2001 (SI 2001 No. 4005) points out that those in the retail and antique trade need to know what radioactive substances are on their premises and in what quantity. UK dealers in our experience are rarely aware of this obligation. In contrast to the UK, in France it is not possible to buy and sell such artefacts via online retailers (Perrier pers comm.). The French National Agency for Radioactive Waste Management recommends that legacy items are not handled directly and that prolonged contact is avoided (ANDRA, 2009, p.31). Interestingly, online retailers such as eBay state that their policy on buying and selling such items “differs from site to site depending upon the laws and regulation of that particular country” (eBay pers comm.). Also, eBay states that (a) buyers and sellers are personally responsible for complying with all laws and regulations and (b) that it is the

individual who is responsible for the legality of the item concerned (see eBay User Agreement, 2015).

Conclusion.

A collection of radium-dial pocket and wrist watches has been shown to be capable of giving rise to radon concentrations two orders of magnitude greater than the UK Domestic Action Level of 200 $Bq \bullet m^{-3}$ in unventilated or poorly ventilated rooms. Furthermore, individual watches are capable of giving rise to radon concentrations in excess of the UK Domestic Action Level.

Radium-dial watches are potentially harmful to health and we would argue that the ALARA principle should be followed wherever such items are concerned. Radium-dial watches and other man-made artefacts incorporating uranium and radium should be included in protocols and guidelines where the generation of radon is concerned.

Radium painted aircraft instrument dials can also clearly be a health hazard in terms of radon potential as shown by our preliminary work, as reported here. Where uranium glass is concerned we would agree with Hansen and Moss (2015) who recommend that further investigation of this source takes place. Lastly, uranium glazes can pose a health risk and give rise to (slightly) raised atmospheric radon. Our own tests to date show then that there is a case for further investigation of other sources of anthropogenic radon (and thoron) other than radium watch (and clock and instrument) dials, but that radioluminescent items such as dial should be treated with particular caution.

Figure captions.

Figure 1. Radioactive decay in Thorium and Uranium Series.

Figure 2. Radium-dial wrist and pocket watches. UK and Swiss made. Radium-dial aircraft altimeter (Mark XIII C No. 1862/40), reportedly from a WWII Spitfire. Red Fiesta ware art deco teapot, made in the USA. Uranium glass dish and lid, 1930s, UK. Radium cigarettes box.

Figure 3. Schematic Diagram of Closed-Loop Measurement System.

Figure 4. Typical measured and modelled radon concentration, for the Helvetia wrist watch. The vertical dashed lines indicate the 144-hour period, 7-150 h.

Table captions.

Table 1. Radon Activity (at equilibrium in test volume).

Table 2. Effective radium content (for watches).

Table 3. Preliminary radioactivity results for various radium- and uranium- containing artefact and ornaments.

Table 4. Provisional radon activity.

Table 5. Preliminary thoron activity.

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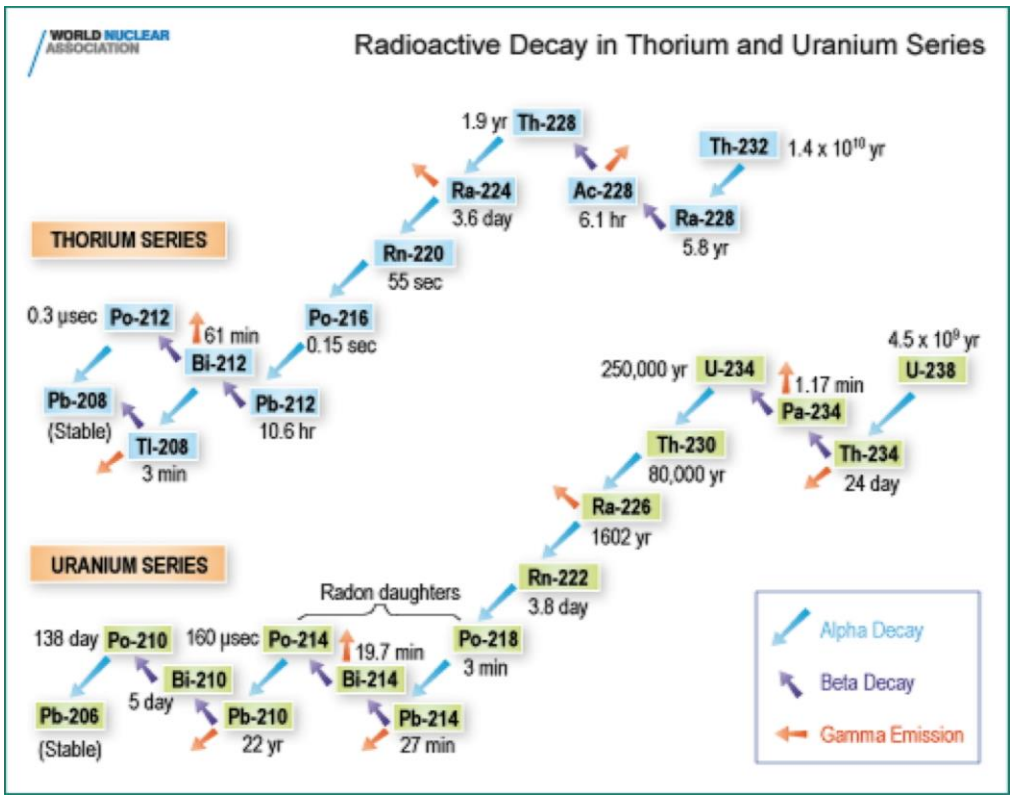
WORLD NUCLEAR ASSOCIATION
Radioactive Decay in Thorium and Uranium Series
THORIUM SERIES
Th-232
1.4 x 10^10 yr
Ra-228
5.8 yr
Ac-228
6.1 hr
Th-228
1.9 yr
Ra-224
3.6 day
Rn-220
55 sec
Po-216
0.15 sec
Pb-212
10.6 hr
Bi-212
61 min
Po-212
0.3 µsec
Tl-208
3 min
Pb-208
(Stable)
URANIUM SERIES
U-238
4.5 x 10^9 yr
U-234
250,000 yr
Pa-234
1.17 min
Th-234
24 day
Th-230
80,000 yr
Ra-226
1602 yr
Rn-222
3.8 day
Radon daughters
Po-218
3 min
Po-214
160 µsec
Bi-214
19.7 min
Pb-214
27 min
Po-210
138 day
Bi-210
5 day
Pb-210
22 yr
Pb-206
(Stable)
Alpha Decay
Beta Decay
Gamma Emission

Figure for Radium and Uranium artefacts paper

Figure 2. Radium dial wrist and pocket watches. UK and Swiss made. Radium dial aircraft altimeter (Mark XIII C No. 1862/40), reportedly from a WWII Spitfire. Red Fiesta ware art deco teapot, made in the USA. Uranium glass dish and lid, 1930s, UK. Radium cigarettes box.

Figure 3. Schematic Diagram of Closed-Loop Measurement System (arrows show direction of air circulation in loop).

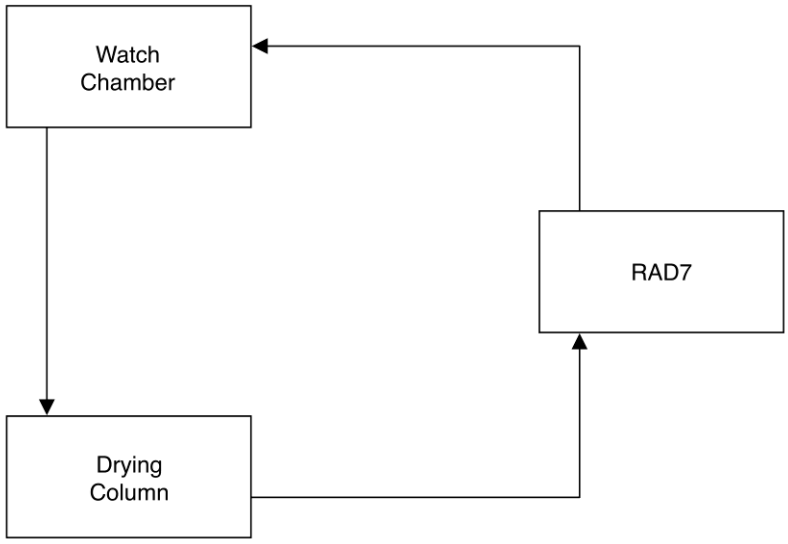

Figure 4. Typical measured and modelled radon concentration, for the Helvetia wrist watch.

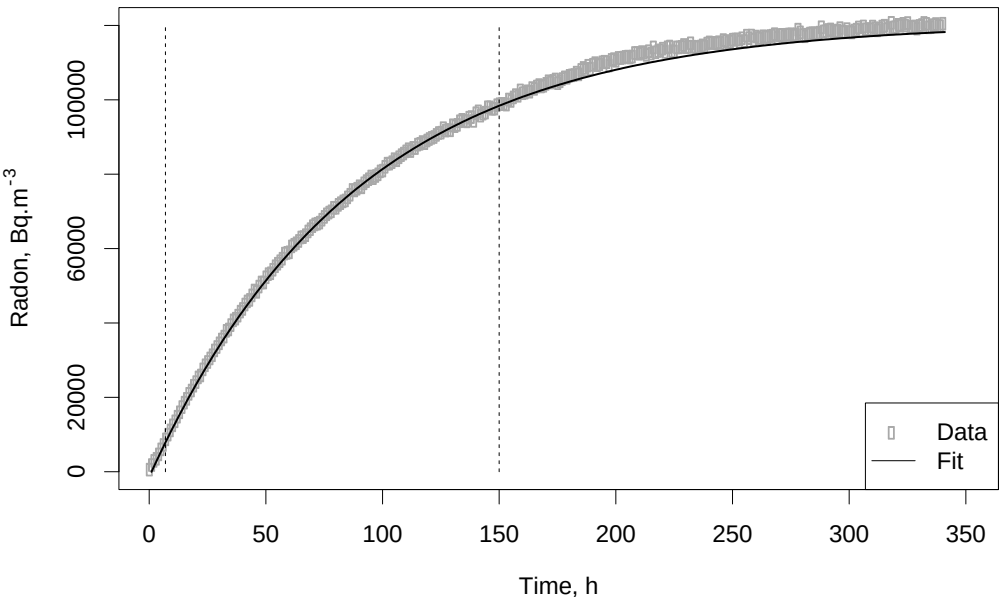

Table 1. Radon activity.

Watch	Leak rate (h^{-1})	Equilibrium		Effective Activity (Bq)	Equilibrium in Hypoth. Room ($Bq•m^{-3}$)	Watch ref. to previous paper
		with leak ($Bq•m^{-3}$)	zero leak ($Bq•m^{-3}$)			
Cyma	0.0053	1403000	2384897	20700.9	1269.0	P3
Helvetia	0.0038	120800	180874	1570.0	96.2	W9
Ingersoll Wrist	0.0024	31490	41530	360.5	22.1	W11
Moeris	0.0056	296700	515345	4473.2	274.2	W13
Newmark 1	0.0065	26240	48669	422.4	25.9	W14
Newmark 2	0.0080	220300	453515	3936.5	241.3	W15
Subset 1	0.0051	578900	973317	125733.0	7707.6	–
Subset 2	0.0043	454300	711499	91911.5	5634.3	–
Collection	–	–	1684816	217644.5	13341.9	–

Table 2. Effective radium content.

Watch	Inferred radium content (Bq)	Effective radium content (Bq)	Ratio of effective to inferred radium content	Watch ref. to previous paper
Cyma	20813	20701	99.5%	P3
Helvetia	3469	1570	45.3%	W9
Ingersoll Wrist	463	360	77.9%	W11
Moeris	32375	4473	13.8%	W13
Newmark 1	2313	422	18.3%	W14
Newmark 2	6938	3937	56.7%	W15
Subset 1	183150	125733	68.7%	–
Subset 2	205582	91911	44.7%	–
Collection	388732	217644	56.0%	–

Table 3. Preliminary radioactivity results for various radium- and uranium- containing artefact and ornaments.

Item	MINI 900 44b (cps)	RadEye B20 (cps)	RadEye B20 ($\mu Sv•h^{-1}$)
Altimeter	>5000	1060.0	185.0
Zenith bedside clock	>5000	785.0	165.0
Cyma bedside clock	380	248.0	44.0
Fiesta-ware teapot, body	300	730.0	110.0
Fiesta-ware teapot, lid	–	560.0	–
Uranium glazed ceramic fragment	200	221.0	38.0
Green uranium glass dish	30	21.2	3.3
Yellow uranium glass fragment	25	14.5	3.0
Granite door-stop	20	2.6	0.54

Table 4. Provisional radon activity.

Object	Leak rate (h^{-1})	Equilibrium		Effective Activity (Bq)	Equilibrium in Hypoth. Room ($Bq \cdot m^{-3}$)
		with leak ($Bq \cdot m^{-3}$)	zero leak ($Bq \cdot m^{-3}$)		
Altimeter	0.0060	467500	836149	108014	6621.4
Granite door-stop	0.0012	5474	6345	55	3.4

Table 5. Preliminary thoron activity.

Object	Leak rate (h^{-1})	Equilibrium		Effective Activity (Bq)	Equilibrium in Hypoth. Room ($Bq \cdot m^{-3}$)
		with leak ($Bq \cdot m^{-3}$)	zero leak ($Bq \cdot m^{-3}$)		
Subset 1	0.0051	17800.0	17802.0	2299.7	140.97
Subset 2	0.0043	13400.0	13401.3	1731.2	106.12
Collection	–	31200.0	31203.3	4030.8	247.10
Altimeter	0.0060	701.0	701.1	90.6	5.55
Granite door-stop	0.0012	83.3	83.3	10.8	0.66
Uranium glass dish	0.0009	20.7	20.7	2.7	0.16