

半挥发性有机污染物的人体暴露评估方法

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摘要 半挥发性有机物(SVOCs)的人体暴露研究已成为环境研究领域的热点。传统的人体暴露评估方法(如血液组织检测等)具有侵入性、复杂性、成本高、样品难获得等缺点。新型被动采样方法以其非侵入性、简单易行、易于接受等优点逐渐受到了广泛关注。总结了非饮食人体暴露评估的方法,重点介绍了人体暴露评估的新兴被动采样技术,包括硅胶腕带、硅胶胸针、手擦拭样、衣服等,其中硅胶手环和硅胶胸针以其廉价易得、易于被接受和稳定性好等优点逐渐得到了广泛应用;此外,利用衣服作为SVOCs人体暴露研究的手段,也具有良好发展潜力和应用前景。

关键词 人体暴露;被动采样;硅胶腕带;衣服;SVOCs

人体暴露,是指污染物经由空气、水、食物和灰尘等途径进入人体的过程。人体暴露评估是指对进入人体的污染物的量化,是人体健康风险评估的重要组成部分。人体暴露研究的目标污染物主要包括:重金属、挥发性有机物(VOCs)和半挥发性有机物(SVOCs)。近些年来,SVOCs的人体暴露研究逐渐受到重视,特别是有机阻燃剂及增塑剂。SVOCs是指沸点在240~400°C且蒸气压在 $(10^{-14} \sim 10^{-4}) \times 10^5$ Pa的有机物^[1-3]。由于具有半挥发性,SVOCs可以通过挥发进入各种环境介质(如空气、

灰尘),并且由于其亲脂性^[4-5],易于人体富集。此外,许多SVOCs具有生殖毒性、神经毒性和致癌作用^[6-8],严重危害人体健康,因此,SVOCs人体暴露的数据亟待完善。与VOCs相比,SVOCs污染来源广泛,组成复杂,难以降解,且暴露途径多样。由于人类活动的复杂性和多样性,更显著增加了污染物人体暴露的不确定性。因此,SVOCs人体暴露评估的难点是区分不同暴露途径,准确估算其暴露量。

目前,人体暴露研究常用的方法包括人体样本检测和模型预测。人体样本主要包括侵入性的血

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液、组织、乳汁和非侵入性的尿液、汗液等。血液、组织、乳汁的采集涉及科研伦理以及安全性等问题,而尿液、汗液等虽不具侵入性,但也涉及受试者的隐私,与侵入性样品一样难以获取。人体样本志愿者的招募困难,涉及科研伦理问题,程序复杂;所获得数据为人体负荷量,和暴露量并不完全一致,且污染物进入人体后会在体内积累,一般不能鉴别人体暴露来源与途径;人体样品采集时,很难控制个体间(interindividual)和个体内(intraindividual)的差异,因此也会影响污染物暴露值的准确性;另外,污染物的毒性代谢动力学和暴露时间也会影响生物标志物的浓度^[9-11]。模型预测是指基于环境介质(空气或灰尘)中污染物浓度或人体直接接触的污染物浓度,利用公式估算人体暴露值的方法。

由于侵入性样本采集的复杂性,利用模型预测人体暴露的方法被研究者广泛应用。然而,对于全暴露途径的模型预测需要大量介质(如食物、饮用水和空气等)的观测数据,且当前研究所用暴露参数大多基于欧美人群,外推至其他人群时可能有所偏差。因此,如何通过改进监测手段提高污染物人体接触量测定的快捷性和准确性,完善参数数据,是提高模型预测结果可靠性的关键。主动空气采样器由于流量已知,能够提供可靠的污染物浓度测量值^[12-13],但通常主动采样器体积较大,无法随身携带,需要持续能源供给,操作相对复杂,需要对受试者进行培训,由于其噪声很大,影响受试者正常生活,因此并不适合个体暴露研究^[13-14]。Nguyen等^[15]设计了可佩戴的便携式的主动空气采样器,采样口悬挂于靠近鼻处,可采集个体的呼吸样本,从而监测污染物的呼吸暴露量;但该采样器仍旧存在成本较高、志愿者难以招募等问题。相比之下,被动采样具有轻便、无需电源、成本低、操作简单、志愿者易招募等特点^[14,16]。因此被动采样器在个体暴露的研究中有着广泛的应用前景。本文介绍几种SVOCs非饮食人体暴露的评估方法,着重介绍非侵入性样本人体暴露的研究进展,特别是几种用于SVOCs非饮食人体暴露研究的新兴被动采样方法。

1 基于环境介质中污染物浓度评估人体暴露量

1.1 基于空气中污染物浓度的人体暴露评估

进入空气中的SVOCs以气态或颗粒态的形式存在,可通过呼吸作用、灰尘摄食、皮肤暴露等途径进入人体,危害人体健康^[17-18]。人体对气态污染物的暴露途径主要有呼吸暴露和皮肤接触,通过呼吸和皮肤接触的污染物平均日暴露量(life-time average daily doses, ADD或LADD)计算公式^[19]为

$$ADD_{\text{inhalation}} = \frac{C_a \times IR \times EF \times ED}{AT \times BW} \quad (1)$$

$$ADD_{\text{dermal}} = \frac{C_a \times EF \times ED \times SA_a \times K_p}{AT \times BW} \quad (2)$$

式中, $ADD_{\text{inhalation}}$ 为通过呼吸的污染物平均日暴露量; ADD_{dermal} 为通过皮肤接触的污染物平均日暴露量; C_a 为空气中污染物的浓度, ng/m^3 ; IR 为吸入速率, m^3/d ; EF 为暴露频率, d/a ; ED 是暴露持续时间, a ; AT 为平均暴露时间, d ,成人设定为24岁,儿童为6岁; BW 为体重, kg ; SA_a 为与暴露于空气的皮肤表面积, cm^2 ; K_p 为污染物的皮肤渗透系数, m/d 。相关参数见表1。

表1 呼吸暴露参数

参数	数值	
	儿童	成人
平均总时长 AT/d	365×	365×
平均体重 BW/kg	6 ^[21]	24 ^[21]
空气吸入速率 $IR/(\text{m}^3 \cdot \text{d}^{-1})$	24 ^[22]	70 ^[23]
暴露于空气的皮肤表面积 $SA_a/(\text{cm}^2 \cdot \text{d}^{-1})$	10.1 ^[19]	15.7 ^[19]
皮肤渗透系数 $K_p/(\text{m} \cdot \text{d}^{-1})$	2040 ^[19]	5570 ^[19]
	144 ^[24-25]	144 ^[24-25]

根据美国环境保护署(EPA)手册,儿童和成人在户外的时间分别占总时长的10%和20%^[20],因此,对于室外暴露的计算可认为,成人的 ED 为 $24 \times 0.2 \text{ a}$,儿童为 $6 \times 0.1 \text{ a}$;对于室内暴露,成人的 ED 为 $24 \times 0.8 \text{ a}$,儿童为 $6 \times 0.9 \text{ a}$ 。

1.2 基于灰尘中污染物浓度的人体暴露评估

灰尘由于比表面积大,是各种有机污染物的良

好载体,在污染物从空气到其他环境基质的运输和分配中起着重要作用^[26-28]。室内灰尘不但可以反映室内环境污染物的污染状况^[29-30],同时也是人体暴露的重要途径^[31]。近年来,室内灰尘中SVOCs的污染特征及人体暴露研究逐渐受到重视^[32-35]。室外灰尘中SVOCs浓度虽然低于室内灰尘,但在交通繁忙的城市地区,街尘中SVOCs的人体暴露也不容易忽视^[36]。灰尘中SVOCs可通过(经手-口)直接摄入、呼吸吸入和皮肤接触进入人体。各暴露途径污染物的平均日暴露量ADD可通过如下公式计算^[19]:

$$ADD_{\text{ingestion}} = \frac{C_d \times R_{\text{ing}} \times EF \times ED \times CF}{AT \times BW} \quad (3)$$

$$ADD_{\text{inhalation}} = \frac{C_d \times R_{\text{inh}} \times EF \times ED}{AT \times BW \times R_{\text{PE}}} \quad (4)$$

$$ADD_{\text{dermal}} = \frac{C_d \times SA_d \times ABF \times AF \times EF \times ED \times CF}{AT \times BW} \quad (5)$$

式中, $ADD_{\text{ingestion}}$ 为通过摄入的污染物平均日暴露量; C_d 为灰尘中污染物的浓度,ng/g; R_{ing} 为灰尘摄入速率,mg/d; CF 为转换因子, 1×10^{-6} kg/mg; R_{inh} 为灰尘吸入速率, m^3/d ; R_{PE} 为颗粒物释放因子, m^3/kg ; SA_d 为暴露于灰尘皮肤表面积, cm^2 ; ABF 为皮肤吸收因子; AF 为灰尘对皮肤的附着力,mg/ cm^2 。相关参数见表2。

表2 灰尘暴露参数

参数	数值	
	儿童	成人
皮肤吸收因子 ABF	0.001 ^[37]	0.001 ^[37]
灰尘对皮肤附着力 $AF/(\text{mg} \cdot \text{cm}^{-2})$	0.2 ^[38]	0.07 ^[38]
平均总时长 AT/d	365×6 ^[21,39]	365×24 ^[21,39]
平均体重 BW/kg	24 ^[22]	70 ^[19,40]
转换因子 $CF/(\text{kg} \cdot \text{mg}^{-1})$	1×10^{-6} ^[41]	1×10^{-6} ^[41]
灰尘摄入速率 $R_{\text{ing}}/(\text{mg} \cdot \text{d}^{-1})$	60 ^[19,40]	30 ^[19,40]
灰尘吸入速率 $R_{\text{inh}}/(\text{m}^3 \cdot \text{d}^{-1})$	7.63 ^[41]	12.8 ^[41]
颗粒物释放因子 $R_{\text{PE}}/(\text{m}^3 \cdot \text{kg}^{-1})$	1.36×10^9 ^[38]	1.36×10^9 ^[38]
暴露于灰尘的皮肤表面积 $SA_d/(\text{cm}^2 \cdot \text{d}^{-1})$	2800 ^[38]	5700 ^[38]

2 基于被动采样研究人体暴露

基于环境介质中SVOCs浓度,通过模型计算

人体暴露的方法,受模型参数的影响,评估结果往往反映的是某一人群的平均暴露量,不能准确反映个体暴露的实际情况。基于被动采样的人体暴露研究,由于实现了原位监测,其结果更准确、可靠。

2.1 非侵入性生物样本

2.1.1 头发和指甲

血液等侵入性样本往往只能反映污染物的近期暴露状况,而头发作为一种非侵入性样本,可以提供长期的综合的暴露状况^[42-43]。由于头发具有易于采集、储存和运输,稳定性好等优点,作为替代性生物标志物被广泛应用^[44-45]。头发中污染物具有双重来源,血液的掺入是其重要的内部来源,灰尘、空气和护发产品是其外部来源^[46]。近些年,头发被广泛应用于SVOCs(特别是阻燃剂)的暴露研究中^[42,47-50]。头发中污染物的浓度可以区分具有不同暴露水平的受试者群体,即对于不同暴露水平的受试者,其头发中污染物浓度有显著不同^[48,51-52]。此外,Liu等^[45]研究发现头发中的多溴联苯醚(PBDEs)水平与血清中的PBDEs水平显著相关。另有研究发现,头发中的三(1,3-二氯-2-丙基)磷酸酯(TDCIPP)和磷酸三苯酯(TPHP)浓度与尿中其相应代谢产物含量显著相关^[47,53-54]。头发作为一种新兴的人体暴露监测手段,也存在一定缺陷,如难以区分内暴露(internal exposure)和外暴露(external exposure),同时头发颜色、长度、与发根距离以及洗发、染发、护发等均可能会产生影响^[44,55-56]。

指甲也可以提供综合的暴露状况,并有很好的稳定性、易于采集和运输,具有作为SVOCs人体暴露的非侵入性生物标志物的潜力^[45]。由于指甲母质和指甲床周围具有丰富的血管和淋巴组织,对化学物质具有很高的渗透性^[43],并且指甲生长速度缓慢,因此可以很好地反映污染物的长期暴露状况^[29,48,57-58]。研究表明:指甲样品中的PBDEs水平与血清中的PBDEs水平显著相关;与头发相比,指甲可能是PBDEs人体暴露的一种更好的非侵入性生物标志物^[45]。Zhao等^[59]在指甲样品均检测到了十溴联苯醚(BDE-209),并指出指甲可以用于预测加工工人血清中BDE-209的浓度。Chen等^[60]研究发现:指甲和灰尘中具有相似的有机磷阻燃剂(OP-

FRs)水平,且2, 2, 4, 4-四溴联苯醚(BDE-47)、磷酸三(2-丁氧基)乙酯(TBOEP)和TBPH在指甲与灰尘样品中的水平具有显著相关性。手指甲和脚趾甲可分别指示特定的(specific)暴露状况^[43],但相比之下脚趾甲能更好地反映污染物的内部暴露状况^[61]。

2.1.2 皮肤擦拭采样

手擦拭样可以捕获通过手-口接触和皮肤吸收造成的暴露^[25,62],其反映的是受试者短期的暴露状况^[31]。研究表明,手擦拭样品中的OPFRs、邻苯二甲酸酯(PAEs)、新型溴代阻燃剂(NBFRs)和多环芳烃(PAHs)的含量与硅胶腕带中的含量正相关^[63]。手擦拭样品中部分OPFRs和PBDEs的浓度与尿液或血液样品中的母体或代谢物浓度呈正相关^[31,53,64-66]。TCIPP(磷酸三(1-氯-2-丙基)酯)和TDCIPP在手擦拭样品中的含量与在室内灰尘中的含量也密切相关^[31]。目前,手擦拭样已被视为测量OPFRs和PAEs人体暴露水平的可靠工具^[53,67]。Phillips等^[68-69]认为利用手擦拭样研究OPFRs的人体暴露要优于利用室内灰尘进行评估。Liu等^[70]认为手擦拭样特别适用于比较不同职业和生活方式人群的暴露差异,然而他也指出,使用手擦拭样评估皮肤吸收暴露量时可能会低估实际的暴露风险,因为其仅包括了通过手部皮肤接触的暴露。儿童手擦拭样中OPFRs的浓度与洗手频率有关,且室内温度与手擦拭样中OPFRs的含量成反比^[66]。手擦拭样对评估儿童的暴露可能会更有效,因为儿童比成人的手-口接触更多,而这种暴露途径可直接被手擦拭样捕获^[62]。

除了手擦拭研究外,Gong等^[71]发现,身体不同部位擦拭样中的污染物浓度显著不同,夏季邻苯二甲酸二(2-乙基)己酯(DEHP)水平为:手掌>手背>前臂>前额,而冬季DEHP水平:手掌~手背>前额>前臂~后背>小腿。Cao等^[72]认为前额是反映人体皮肤对雾霾中OPFRs暴露的最佳位置,并采用前额擦拭样进行了雾霾的人体暴露评估。

2.2 硅胶被动采样器

硅胶(silicone)或聚二甲基硅氧烷(polydimethylsiloxane, PDMS)具有极强的有机污染物吸附能

力,包括从挥发性苯、甲苯和二甲苯到更具亲水性的含有羟基、酮或羧基的有机污染物。有机污染物接触到硅胶后,不仅会吸附到表面,还会随着时间的推移被吸收并渗透到整个材料中^[73]。因此硅胶是一种良好的被动采样材料,被广泛应用于野外大气或水体被动采样。近年来,有学者利用商品化或自制硅胶腕带(手环)或胸针开展经呼吸、灰尘摄入或皮肤接触的人体暴露研究^[74]。

2.2.1 硅胶腕带

硅胶腕带因其小巧轻便、廉价易得和易于被接受等优点,已经被广泛应用于各种污染物的检测。研究表明,硅胶腕带可以捕获辛醇-空气分配系数($\lg K_{oa}$)在2.1~13.7范围内的有机污染物^[13,75]。迄今为止,已利用硅胶腕带研究了1500多种化学物质,包括OPFRs^[31,63,73]、PAEs^[62,76]、PAHs^[9,77]、个人护理产品中使用的化学药品^[74,78]和农药^[79-80]。硅胶腕带由于随身佩戴,可以捕获包括来自空气、灰尘,甚至是个人护理产品中的有机污染物,因此更能体现受试者个人污染物的总体暴露状况^[9,73];此外也可捕获多种暴露途径,包括在呼吸、手-口摄入和皮肤接触,对全面评估个体暴露状况有着广泛的应用前景^[81]。多项研究发现,腕带上积累的有机污染物(如TDCIPP、TCIPP和部分多环芳烃等)与血液和尿液中相应的代谢产物之间存在显著相关性^[9,31,62-63,81]。被硅胶腕带捕获的化合物还具有很强的稳定性。Anderson等^[75]的研究表明,在-20℃条件下,硅胶腕带中的化合物在至少能保留6个月。Kile等^[73]的研究表明,硅胶腕带中阻燃剂在-20℃下的稳定性会远远超过84 d,甚至可能长达500 d,在高温(例如30℃)的条件下有机阻燃剂不会降解,这使得硅胶腕带在样品运输和保存方面具有显著优势。虽然硅胶腕带具有诸多优点,但目前还不能区分暴露途径(可能部分来自与皮肤接触所产生的内暴露)和来源;此外,硅胶腕带并不能评估饮食带来的人体暴露风险。

2.2.2 硅胶胸针或胸牌

硅胶胸针(silicone brooch)的采样原理与硅胶腕带相似,但胸针由于佩戴位置更接近于口鼻,因此其结果能够更准确地反映污染物的呼吸摄入量

(包括气态和颗粒态);同时相比腕带,胸针避免了皮肤接触,因此杜绝了内暴露的影响。Okeme等^[14]利用了自制硅胶胸针(PDMS, 9 cm×5.5 cm×0.1 cm)评估了个人的OPFRs和PAEs呼吸暴露,研究表明硅胶胸针可以有效评估低分子量的OPFRs、PAEs、NBRs和PAHs的呼吸暴露,但对高分子量的污染物效果不佳。对于空气中浓度 $>4 \text{ ng}\cdot\text{m}^{-3}$ 且范围在 $\text{ng}/\text{m}^3\sim\text{mg}/\text{m}^3$ 的化合物,硅胶胸针可以捕获24 h以内的吸入暴露量^[14]。此外,Poutasse等^[16]利用宠物硅胶胸牌(silicone tag)研究了宠物猫的TD-CIPP呼吸暴露。

2.3 衣服

衣服覆盖人体约85%的皮肤^[82],对于化学物质的皮肤接触暴露发挥着重要作用^[83-84]。衣物等纺织品由于巨大的比表面积,可以积累空气中有机污染物^[85-87]。然而,SVOCs的空气-衣服分配比通常很大,且与污染物本身 K_{oa} 有关,因此室内环境中衣服积累SVOCs的速度较慢^[88]。纺织品对不同理化性质的化合物的积累能力不同,更易积累 K_{oa} 较高的污染物^[89]。研究表明,洁净的衣物对污染物人体暴露具有阻隔作用,可以降低暴露量;一旦衣物吸收了大量污染物,则会显著增加污染物的皮肤暴露量^[71,90-92]。Wang等^[93]首次利用纯棉T恤作为被动采样材料,研究了孟加拉地区电子废物拆解工人的OPFRs和溴代阻燃剂(BFRs)的人体暴露量。其研究发现,T恤和硅胶腕带中部分OPFRs和BFRs浓度存在显著正相关性^[93];相比光滑的硅胶腕带,T恤具有粗糙的纹理,能更有效地捕获颗粒态的有机污染物^[89]。

3 结论

随着人们对自身健康的关注越来越高,人体暴露研究逐渐成为环境领域研究热点,而方便可行的监测技术和手段是人体暴露研究亟待解决的关键问题。头发、指甲虽然不具有侵入性,但志愿者招募仍然困难;硅胶手环、胸针和手擦拭样,操作简单、廉价易得、采样方便、结果相对可靠,已成为目前理想的非侵入性监测手段。衣物等纺织品由于

材料廉价、样品易获得等特点,在人体暴露研究方面具有良好的应用前景。未来,人体暴露的评估手段应更加着眼于非侵入性、易于实施、成本低、样本稳定性好、易于保存等特点。另外,也应着力于对新型采样方法和监测手段的开发和验证、采样材料的创新、人体暴露模型的开发与完善、相关参数的优化等方向,以便进一步提高SVOCs人体暴露评估的可靠性,从而为防范人体健康风险提供理论基础和技术支持。

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Assessment of human exposure to semivolatile organic pollutants

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Abstract The assessment of the human exposure to the semivolatile organic compounds (SVOCs) is one of the hotspots in the environmental research field. The traditional methods (such as the blood and urine tests) have the disadvantages of invasiveness, complexity, high cost, and difficulty in collecting samples, among others. Novel passive sampling technologies were developed, which are non-intrusive, simple and convenient, and practicable. This paper reviews the human exposure assessment methods, including the model calculation based on the SVOC concentrations in the environmental matrices (e.g., air or dust), the invasive sampling, and the passive sampling, focusing on the emerging novel passive sampling technologies, including the silicone wristband, the silicone brooch, the hand wipe, and the clothing. Currently, the silicone wristband and brooch and the hand wipe samplings are widely used due to their advantages, such as the low price, the ease to use, the acceptability, and the good stability. The hand wipe can be used to capture the exposures via the hand-to-mouth contact and the dermal absorption. Meanwhile, the clothing is a novel passive sampling technology, which can be used to capture both gaseous and particle SVOCs. Therefore, using clothing to assess the human exposure has a good promise in its development and application.

Keywords human exposure; passive sampling; silicone wristband; clothing; SVOCs ●



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