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影响悬浮颗粒物吸收系数测量的相关因素研究

余小龙,沈芳*,张晋芳

(华东师范大学河口海岸学国家重点实验室,上海 200062)

摘要:水体悬浮颗粒物吸收系数是水色遥感研究中的关键参数之一,为研究不同因素对吸收系数测量结果的影响,分别采用透射法(T法)、透射反射法(T-R 法)和吸收法(A 法)测量颗粒物吸收系数.结果表明,A 法在测量悬浮颗粒物吸收系数时受滤膜差异性、滤膜含水量以及滤膜颗粒物分布不均匀等因素的影响较小,测量精度较高.对不同测量方法的光程放大因子的研究结果表明,不同测量方法,不同颗粒物富集量会有不同的光程放大因子.采用线性拟合的方法求得 A 法、T 法和 T-R 法的平均光程放大因子为4.01、2.32 和2.20,相关系数分别为0.90、0.80 和0.87.对于 A 法和 T-R 法,采用二次多项式拟合的方法计算光程放大因子可以提高测量精度,相关系数分别为0.95 和0.94.对比各影响因素对测量结果造成的平均相对误差发现,光程放大因子是颗粒物吸收系数测量最大的误差来源.

关键词:悬浮颗粒物;吸收系数;T法;T-R法;A法;光程放大因子中图分类号:X87 文献标识码:A 文章编号:0250-3301(2013)05-1745-09

Influencing Factors in Measuring Absorption Coefficient of Suspended Particulate Matters

YU Xiao-long, SHEN Fang, ZHANG Jin-fang

(State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China)

Abstract: Absorption coefficient of suspended particulate matters in natural water is one of the key parameters in ocean color remote sensing. In order to study the influencing factors that affect the measurement, a series of experiments were designed to measure samples using transmittance method (T method), transmittance-reflectance method (T-R method) and absorptance method (A method). The results shows that absorption coefficient measured by the A method has a much lower error compared to the T method and T-R method due to influencing factors, such as filter-to-filter variations, water content of the filter, and homogeneity of filter load and so on. Another factor influence absorption coefficient is path-length amplification induced by multiple scattering inside the filter. To determine the path-length amplification, the true absorption was measured by AC-s (WetLabs). The linear fitting result shows that the mean path-length amplification is much higher for the A method than that of the T-R method and the T method (4.01 versus 2.20 and 2.32), and the corresponding correlation coefficient are 0.90, 0.87 and 0.80. For the A method and the T-R method, higher correlation coefficients are calculated when using polynomial fitting, and the value are 0.95 and 0.94. Analysis of the mean relative error caused by different influencing factors indicates that path-length amplification is the largest error source in measuring the absorption coefficient. Key words:suspended particulate matter; absorption coefficient; T method; T-R method; A method; path-length amplification factor

悬浮颗粒物是水体重要的组成成分之一,悬浮颗粒物的吸收系数也是目前水色遥感中关键参数之一,它在叶绿素浓度反演、悬浮泥沙浓度反演、初级生产力及各种生物光学模型的建立和应用上都有着十分重要的作用. 悬浮颗粒物的吸收系数的实验室测量主要基于定量滤膜技术(quantitative filter technique,QFT)^[1],即通过滤膜富集悬浮状态的颗粒物进行测量. 在测量方法上,Yentsch^[2]在1962年提出了光透射测量法(T法),使得实验室测量悬浮颗粒物吸收系数成为可能. Trüper等^[3]在1967年对该方法进行修改,随后被广泛应用于悬浮颗粒物吸收系数测量上^[4~8],Mitchell^[1]、Cleveland等^[9]采用多项式拟合的方法计算光程放大因子并给出了光程放大因子计算的经验参数,提高了T法测量的精度,但是由于T法不能很好地解决样品滤膜后向散

射问题,使得T法测量存在局限性. 浑浊水体颗粒物的高散射因素对T法测量结果也会造成较大的误差. 为了降低散射等因素的影响,Tassan等[10]提出了透射-反射法(T-R法),通过测量样品滤膜的透射率和反射率,经过计算后有效的降低了散射等因素的影响,随后Tassan等[11]对T-R法测量精度进行分析并对初始的T-R法进行了改进,提高了测量精度,该方法被SeaWiFS计划推荐为悬浮颗粒物吸收系数的测量方法[12],Babin等[13]也采用T-R法进行

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作者简介: 余小龙(1990~),男,硕士研究生,主要研究方向为河口海岸水色遥感,E-mail;yushour@163.com

* 通讯联系人, E-mail:fshen@sklec.ecnu.edu.cn

颗粒物吸收系数测量并取得较高的测量精度.为了进一步消除散射因素的影响,有学者如 Maske 等[14] 将滤膜置于积分球内部进行吸光度的测量,即吸收法(A法),但由于该方法对实验设备要求较高,应用实例较少. 近年来,Babin 等[15] 为了研究悬浮颗粒物在近红外波段吸收,采用 A 法进行测量以降低散射因素的影响,验证了悬浮颗粒物中的无机碎屑等物质在近红外波段吸收不可忽略,这一结论也对T 法的散射校正提供了新的思路. 随后,Babin等[16,17]使用 A 法进行不同固体矿物质的比吸收系数的测量,也取得较好的结果. Röttgers 等[18]针对不同水体,通过大量的实验求出了 A 法计算悬浮颗粒物吸收系数的光程放大因子,并给出了适合的吸光度测量范围,较系统地给出了 A 法应用于水体悬浮颗粒物吸收系数测量和计算方法.

然而,颗粒物吸收系数测量结果不仅与测量方法和光程放大因子有关,还与一些其他的因素有关,如滤膜之间的差异、滤膜水合程度、样品过滤体积和颗粒物分布是否均匀等.这些影响因素对测量结果的影响程度国内外还少有研究.本研究从上述影响颗粒物吸收系数测量的因素着手,通过3种测量方法的对比实验,分析不同影响因素对实验结果的影响,并计算各种影响因素对测量结果造成的误差,对颗粒物吸收系数的测量方法的研究以及提高测量精度有一定的参考价值.

1 仪器和测量方法

所有测试样品的采集方法均参考 NASA 的生物 光学调查规范^[12]和国家海洋局 908 专项办公室编制的海洋光学调查技术规程^[19]. 首先采集水样置于阴暗处,将空白 GF/F(Whatman™ Φ47 mm)滤膜浸泡在蒸馏水中 60 min 以上,过滤一定体积(V_r)水样到 GF/F 滤膜上,同时过滤蒸馏水作为参比样品,过滤完成后置于贴有标签的样品盒,滴加一滴蒸馏水后转移至液氮桶保存. 测量采用的仪器主要有测量悬浮状态下水体吸收系数的吸收衰减仪(AC-s,WetLabs)以及实验室测量样品滤膜吸收的双光束紫外可见分光光度计(Lambda-1050,Perkin Elmer),其中,Lambda-1050 带有 150 mm 直径的积分球. 积分球内壁具有耐用的高反射朗伯材料 Spectralon 涂层和 Spectralon 漫反射板.

本研究主要介绍 A 法的测量方法,透射法和透射反射法的测量方法参照海洋光学调查技术规程^[19]. A 法的测量方法如下:测量前将仪器预热 30

min 以上,并在测量样品前进行 100% T 和 0% T 校正. 将仪器调至吸收模式,将滤膜去除多余水分后置入积分球内,调节支架角度,使得样品滤膜富集颗粒物一面正对样品光入射方向,同样方法测量一张空白滤膜作为参比. A 法颗粒物吸收系数计算公式如下:

$$a_{p}(\lambda) = \frac{2.303A_{f}}{\beta V_{f}} [D_{s}(\lambda) - D_{r}(\lambda)] \qquad (1)$$

式中, $A_{\rm f}$ 和 $V_{\rm f}$ 分别为滤膜上颗粒物富集面积和过水体积; $D_{\rm s}(\lambda)$ 为样品滤膜光学密度; $D_{\rm r}(\lambda)$ 为空白参比滤膜的光学密度, β 为光程放大校正因子.

2 结果与分析

2.1 空白滤膜的差异性

研究发现,即使同一批次的 GF/F 滤膜,其光学特性也有一定的差异,而预浸泡能够有效地降低滤膜之间的差异^[12].为了研究空白滤膜水合程度对光学特性的影响,随机抽取同一批次 GF/F 滤膜 5 张,浸泡在蒸馏水中,每隔 20 min 取出滤膜,然后分别使用 T 法和 A 法测量空白滤膜相对空气的光学密度,滤膜取出时间间隔为 0 (dry)、20、40、60、80、100、120 min,采样波长为 300~900 nm,采样间距 5 nm. 文中采用各测量时刻 5 张滤膜吸光度的标准偏差作为指标来指示滤膜之间的差异性,计算结果如图 1.

从 T 法测量结果[图 1(a)]可以看出,不同的空白滤膜之间存在一定的差异性,滤膜之间的差异性随着浸泡时间逐渐降低,浸泡 60 min 后,滤膜之间的差异性明显降低. 对于 A 法来说[图 1(b)],各测量时刻空白滤膜的差异性不显著. 为了更方便观测各时刻空白滤膜的差异性,笔者把各时刻测量结果的标准偏差以表格形式给出,见表 1.

表 1 各测量时刻可见近红外波长范围空白滤膜之间的 标准偏差变化范围以及平均标准偏差¹⁾

Table 1 Range and standard deviation of the values measured for the blank filters in visible and near infrared spectral ranges at different soaking time

浸泡时间 /min		透射法	吸收法	
	0 (dry)	0.0030 ~ 0.0096(0.0064)	0.0001 ~ 0.0019(0.0004)	
	20	0.0062~0.0094(0.0069)	0.0002 ~ 0.0013(0.0005)	
	40	0.0050 ~ 0.0090(0.0077)	0.0001 ~ 0.0020(0.0005)	
	60	0.0043 ~ 0.0064(0.0048)	0.0001 ~ 0.0015(0.0003)	
	80	0.0029 ~ 0.0051(0.0042)	0.0001 ~ 0.0009(0.0003)	
	100	0.0016~0.0045(0.0035)	0.0002~0.0011(0.0005)	
	120	0.0018~0.0043(0.0032)	0.0001~0.0012(0.0004)	

1)括号内数据为平均标准偏差

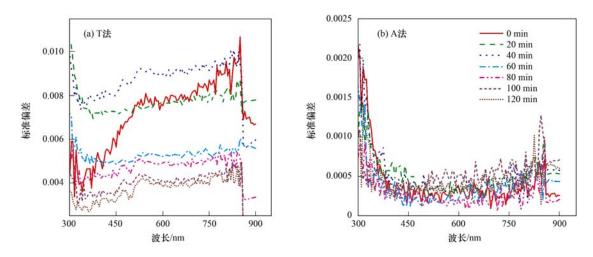


图 1 各测量时刻 T 法和 A 法测量 5 张空白滤膜吸光度的标准偏差

Fig. 1 Standard deviation of the optical density measured for 5 blank filters at different soaking time using the T method and the A method

由表 1 可发现, A 法受滤膜差异性影响较小, 在可见近红外波长范围都有较低的标准偏差, 平均标准偏差小于0.000 5, 而透射法测量结果的平均标准偏差则基本位于0.003 2~0.007 7之间. 故建议 T 法测量时在过滤样品前将 GF/F 滤膜浸泡 60 min 以上,这一结果与 Bricaud 等^[20]以及朱建华等^[21,22]得出的结论近似. 由于 GF/F 滤膜是由玻璃纤维压制而成,长时间浸泡会使玻璃纤维蓬松,改变原先滤膜的散射特性,因此 T 法测量时推荐过滤颗粒物吸收样品前将滤膜浸泡 60~120 min. A 法测量时滤膜受浸泡时间影响较小,一般也选择 60 min 左右^[18].

2.2 滤膜含水量对测量结果的影响

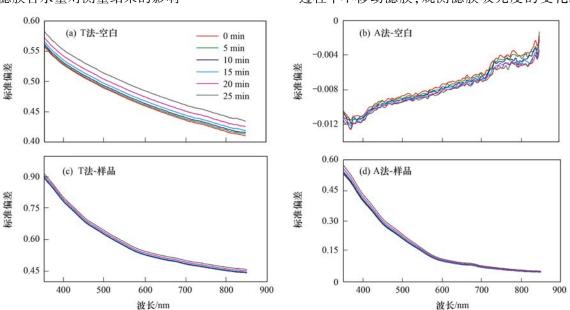


图 2 不同时刻(含水量降低)空白滤膜与样品滤膜吸光度的变化
Fig. 2 Variations in optical densities of blank filters using the T method and the A method and sample filters using the T method and the A method with water content decreasing

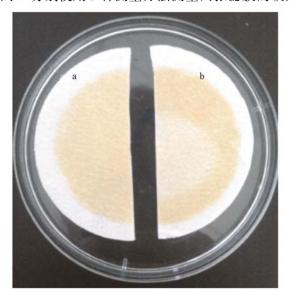
定量滤膜技术(QFT)测量悬浮颗粒物吸收系数时滤膜的水合程度往往难以控制到相同水平,因此水分的含量也会对测量结果造成一定的影响.本研究通过 T 法和 A 法对空白滤膜以及若干样品滤膜进行滤膜含水量变化对测量结果影响的实验,样品为自然水体(丽娃河水体和崇明东滩近岸水体)过滤得到.测量方法为分别以 T 法和 A 法测量空白滤膜或者样品滤膜的吸光度(时刻为 0 min),采样范围350~850 nm,采样间隔 2 nm(下文实验测量均采用该采样范围和间隔),然后每隔 5 min 进行一次扫描,随着时间推移,滤膜上含水量会逐渐减少,测量过程中不移动滤膜,观测滤膜吸光度的变化.图 2

为空白滤膜和样品滤膜的测量结果(限于篇幅,仅显示两个样品滤膜的结果).

由图 2 可以发现,T 法与 A 法表现出相同的变化规律,随着滤膜含水量的减少(时间增加),空白滤膜与样品滤膜的吸光度总体呈增加趋势,这一现象与 Roesler^[23]得出的实验结果相同.图 2(a)和图 2(c)为 T 法测量的空白滤膜和样品滤膜,可发现 T 法测量时滤膜水合程度对空白滤膜的影响较大,图 2(a)平均标准偏差为0.009 4,而对样品滤膜的影响较小,图 2(c)平均标准偏差为0.007 3; A 法测量时空白滤膜[图 2(b)]和样品滤膜[图 2(d)]的平均标准偏差分别为0.000 3和0.006 2.无论 T 法还是A 法,样品滤膜水合程度变化引起的吸光度误差相对于样品整体的吸光度来说都是较低的,因此在实验中采用同样的去除多余水分的操作能够有效地降低滤膜含水量对测量结果的影响.

2.3 滤膜上颗粒物分布均匀性对测量结果的影响

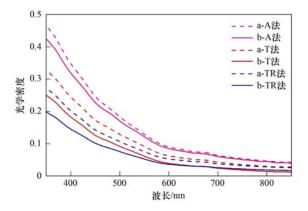
采用定量滤膜技术(QFT)测量时都要求测量之前将水样摇匀,并认为过滤后的滤膜是均匀的,这是计算悬浮颗粒物吸收系数的基本前提和假设. 但在实际过滤样品中,样品滤膜颗粒物分布并不是完全均匀的. 为了研究滤膜均匀性对测量结果的影响,本实验中过滤了相同体积水样的两张滤膜,一张滤膜[图3(a)]为均匀过滤;一张滤膜[图3(b)]为非均匀过滤,悬浮颗粒物中间分布稀薄,过滤后如图3所示. 分别使用3种测量方法测量两张滤膜的吸光



(a) 为均匀分布样品,(b) 为非均匀分布样品 图 3 两张对比滤膜

Fig. 3 Comparison of two filters one is the case of samples in homogenous distribution and the other in non-uniform distribution

度,得到的结果如图 4 所示.



(a) 为均匀分布样品,(b) 为非均匀分布样品

图 4 A 法、T 法和 T-R 法测量两张滤膜对比

Fig. 4 Optical density of the contrastive filters using the A method, the T method and the T-R method

由图 4 可发现:对于 T 法和 T-R 法测量的两条 曲线差异非常明显,而 A 法测量的两条曲线差异相对较小. 计算非均匀过滤样品吸光度相对于均匀过滤样品吸光度的误差,可以发现,T 法误差最大,全波长内吸光度的平均误差为 37.6%,最大误差达到了 58.1%; T-R 法次之,平均误差和最大误差分别为 27.0% 和 35.6%; 而对于吸收法来说,样品的不均匀性对测量结果造成的误差较小,全波长内吸光度的平均误差为 6.3%,最大误差为 9.0%.

分析主要原因为,T 法和 T-R 法测量的样品滤膜位于积分球外部,只在光束穿过样品滤膜的部分产生颗粒物吸收,故要求样品滤膜具有良好的均匀性,由此可近似以部分滤膜上的颗粒物吸光度替代整个滤膜颗粒物吸光度,否则会产生较大误差; T-R 法多次测量可稍微降低误差; 而采用 A 法测量,样品滤膜置于积分球内,样品光束在积分球内壁多次反射使得整个滤膜上的颗粒物都产生吸收,故所测吸光度即为样品吸光度,对滤膜的均匀性要求不是很高.

2.4 T法、T-R法以及 A 法差异性研究

采用前文描述的测量方法,利用 Lambda1050 进行 T 法、T-R 法以及 A 法测量,收集丽娃河水为实验样品,采用 Φ 47 mm GF/F(WhatmanTM) 滤膜过滤水体. 分别使用 3 种测量方法对同一样品滤膜进行测量,得出悬浮颗粒物光学密度($D_{T,T-R,A}$)的特征如图 5 所示.

从图 5(a)中可以发现,对于同一样品 3 种测量方法获得的吸光度之表现为 A 法 > T 法 > T-R 法, 主要原因是 T 法和 T-R 法测量时滤膜位于积分球

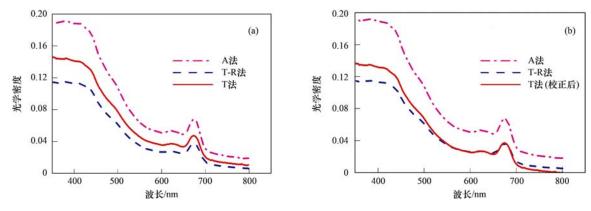


图 5 3 种方法测量吸光度的对比(以一个样品为例)

Fig. 5 Optical density measured by the A method, the T-R method and the T method

外部,但是 T 法不能很好地去除滤膜后向散射的影响,导致后向散射部分的损失计算到吸收中,从而导致测量值相比 T-R 法的略高, T-R 法通过合理的设计多次测量达到了降低散射因素的影响,从而散射影响较小,测量值较 T 法略低. 对于吸收法来说,滤膜置于积分球内部,能够参与吸收的颗粒物较 T 法和 T-R 法多,故整体吸收系数偏高,这也是 A 法光程放大因子与其他两种测量方法不同的原因.

3 种测量方法还有一个比较大的差异是 T 法测 量结果需要进行散射校正.T 法测量时一般以近红 外某一波长处的吸收值或一定波长范围内的平均吸 收值作为零值来进行全波长的校正,本研究采用 790~800 nm 的平均值作为零值吸收校正. 从图 5 (b)可以发现,经残余吸收校正后,T 法和 T-R 法在 400~700 nm 内吻合度较好, 而在 400 nm 之前以及 700 nm 之后表现出较大差异. 主要原因为样品在全 波长的散射影响不一,对比图 5(a) 可以发现,T 法 和 T-R 法在短波差异较大,长波差异较小,在全波 长散射因素的影响近似呈指数衰减下降,因此以近 红外波段某处的吸收作为残余吸收在短波范围并不 适用,表现出 T 法仍大于 T-R 法测量结果. 此外,对 于近岸及内陆湖泊水体,滤膜上富集的颗粒物如细 菌、有机碎屑、无机碎屑等在近红外波长的吸收不 可忽略,T 法以该处的吸收作为零值校正会导致测 量结果整体偏小,尤其对于散射作用较小的长波段 处的吸收,这也正是 T 法校正后在长波的测量结果 较 T-R 法低的原因. 所以,目前 T 法测量时采用的 零值吸收校正方法还是存在较大的不足之处,因此 若能够根据样品吸收波谱特性,建立一个波长依赖 的校正函数进行散射校正会更加合理.

3 种方法测量的结果虽然存在一定的差异,但 是也有一定的相关关系. 本研究计算了3 种测量方 法得出的样品吸收系数($\beta=1$),仅从测量的结果数据分析,可发现 A 法与 T 法和 T-R 法的测量结果存在良好的线性相关关系. 如图 6,以 A 法测量吸收系数为横坐标,T 法和 T-R 法测量吸收系数为纵坐标绘制散点图,对散点进行线性拟合. 由图 6 可得出,A 法测量结果分别与 T 法和 T-R 法测量结果有良好的相关性,相关系数分别为 0.94 和 0.99. 良好的相关性说明 3 种测量方法在测量富集状态下悬浮颗粒物吸收系数具有较高的可重复性,其中 A 法与T 法测量的相关系数较 T-R 法低,分析原因为 T 法测量未能有效去除散射误差,导致在吸收系数计算时存在偏差.

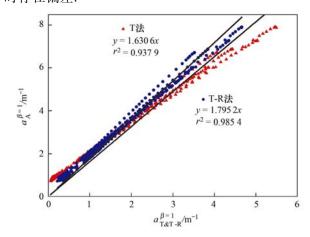


图 6 A 法与 T 法和 T-R 法测量结果的线性关系

Fig. 6 Linear relationship between samples absorption (β = 1) measured by T method, T-R method and A method

2.5 光程放大因子

由于悬浮颗粒物富集在滤膜上的累积效应以及 GF/F 滤膜高散射特性对测量结果的影响,通常在计 算悬浮颗粒物吸收系数时采用光程放大因子对测量 结果进行校正. 光程放大因子的计算方法为样品滤 膜测的吸收(β=1)与悬浮状态下真实吸收的比值. 本研究采用 AC-s 吸收衰减仪(WetLabs, 波长范围 399.8~743.7 nm)测量现场水体真实吸收,分别用 T 法、T-R 法以及 A 法测量样品滤膜的吸收(β=1),为了研究滤膜上颗粒物富集含量与吸收系数之间的关系,采用同一水样分别过滤 50、75、100、150、200 和 300 mL,测得的结果如图 7 所示.

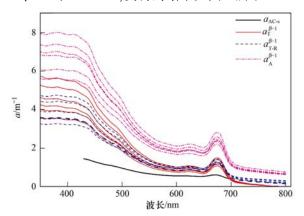


图 7 A 法、T 法、T-R 法和 AC-s 测量的吸收系数

Fig. 7 Absorption coefficients of samples measured by AC-S, $A \ \mbox{method} , \ T\mbox{-R} \ \mbox{method} \ \mbox{and} \ \mbox{T} \ \mbox{method}$

从图 7 中可以发现,3 种测量方法测量的吸收系数($a_{T,T,R,A}^{\beta=1}$)呈现的规律与上节描述相似,并且普遍比真实吸收(图 7,底部黑线)高 2 ~ 5 倍左右.通过 3 种测量方法得出的吸收系数($\beta=1$)与真实吸收的比值可以得到 3 种测量方法的光程放大因子,如图 8,线性拟合的斜率即为每种方法的平均光程放大因子. 从图 8 可得到 A 法、T 法和 T-R 的光程放大因子分别为 4.01、2.32、2.20,对应的相关系数分别为0.90、0.80 和0.87.结果表明 A 法测量

的结果优于 T-R 法,T 法最差. 一般来说,T 法与 T-R 法采用相同的光程放大因子,而 T 法由于散射因素的影响会导致光程放大因子与 T-R 有一定的差异,但差异较小(2.32 与 2.20). 故后面主要分析 A 法和 T-R 法的光程放大因子的计算方法.

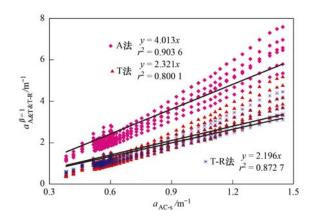


图 8 线性拟合获取 A 法、T 法和 T-R 法的光程放大因子 Fig. 8 Linear regression of the path-length amplification factors from the three methods

以上采用的线性拟合得出的光程放大因子不依赖波长和样品吸光度大小,即在全波长范围内是一个常数.事实上,光程放大因子随着滤膜富集颗粒物的多少会发生变化.对于 T-R 法光程放大因子的计算,除了采用线性拟合外[18],国内外学者大多采用二次多项式的方法进行拟合[1,22,24,25],本研究采用二次多项式方法对真实吸收和 T-R 测量的吸收系数 $(a_{T-R}^{\beta=1})$ 进行了拟合,并与线性拟合结果进行了对比,见表 2.

表 2 T-R 法计算光程放大因子的拟合公式及结果¹⁾

Table 2 Linear and polynomial fitting result for calculating the path-length amplification factor of the T-R method

过滤		线性		二次多项式		
体积/mL	拟合公式	R^2	数据点	拟合公式	R^2	数据点
50	y = 2.55x	0. 885	55	$y = 1.35x^2 + 1.21x$	0. 994	55
75	y = 2.42x	0. 903	55	$y = 1.\ 12x^2 + 1.\ 30x$	0. 994	55
100	y = 2.18x	0. 914	55	$y = 0.93x^2 + 1.26x$	0. 994	55
150	y = 2.00x	0.913	55	$y = 0.86x^2 + 1.15x$	0. 994	55
200	y = 2.07x	0. 947	55	$y = 0.62x^2 + 1.45x$	0. 993	55
300	y = 1.96x	0. 96	55	$y = 0.47x^2 + 1.49x$	0. 993	55
Total	y = 2.20x	0. 873	330	$y = 0.89x^2 + 1.31x$	0. 944	330

1)y 为 $a_{T-R}^{\beta=1}$, x 为真实吸收

从表 2 可发现,采用线性拟合后,光程放大因子为常数,变化范围为 1.96~2.55,光程放大因子随着颗粒物富集含量增多呈减小趋势,平均值为 2.07,与 Röttgers 等^[18]的结果符合(β 为 2.0~3.5,平均值 2.5).采用二次多项式对测量结果进行拟

合后, $a_{T,R}^{\beta-1}$ 与真实吸收拟合的相关性在 0.99 以上,较线性拟合有很大的提升,由此也说明 T-R 法的光程放大因子依赖于样品滤膜的吸光度,故 T-R 测量悬浮颗粒物吸收系数时建议采用二次多项式拟合进行光程放大因子的计算.

对于 A 法的光程放大因子研究,目前国际上还比较少,Röttgers 等^[18]在经过大量实验发现,A 法测量悬浮颗粒物吸收系数的光程放大因子在样品吸光度 D < 0.1 时,不依赖吸光度,即为常量,其取值范围为 β 3.5~6,平均值 4.5; 而 0.1 < D < 0.5 时,光程放大因子应采用二次多项式的方法计算. 文中根据实测数据,首先通过绘制真实吸收系数(a_{AC-s})与A 法测量的颗粒物吸收系数 $a_A^{\beta=1}$ 的散点图并进行线性拟合,拟合曲线如图 9 所示.

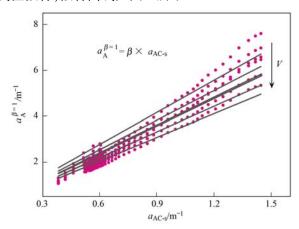


图 9 A 法计算光程放大因子的拟合曲线

Fig. 9 Fitting curve for calculating path-length amplification factor from the A method

表 3 A 法计算光程放大因子的结果¹⁾

Table 3 Linear fitting functions for calculating path-length amplification factor of the A method

	过滤体积/mL	拟合公式	R^2	数据点
	50	y = 4.65x	0. 939	55
	75	y = 4.27x	0. 943	55
	100	y = 4.04x	0. 944	55
	150	y = 3.98x	0. 944	55
	200	y = 3.71x	0. 968	55
	300	y = 3.44x	0. 971	55
_	Total	y = 4.01x	0. 904	330

 $1)y 为 a_A^{\beta=1}, x 为真实吸收$

从图 8 中可以得出,对于不同过水体积的样品滤膜,计算出的光程放大因子并不相同,随着过水体积增大(箭头方向体积增大)光程放大因子呈较小趋势,变化范围 β 为 4.65~3.44,相关系数都在0.939以上,平均光程放大因子拟合值为 β =4.01(图 8),相关系数为 0.90,测得结果与 Röttgers等[18]得出的光程放大因子(β 为 3.5~6,平均值为4.5)具有可比性. 文中也对 A 法测量的吸收系数进行二次多项式拟合,拟合结果的相关性较线性拟合有一定提升,拟合相关系数为 0.95,拟合公式为:

$$a_{\rm A}^{\beta=1} = 1.148 a_{\rm AC-s}^2 + 2.876 a_{\rm AC-s}$$
 (2)

已有研究表明,不同藻种的光程放大因子存在 较大差异[1,10,25~27],本研究采用 T-R 法和 A 法测量 的光程放大因子结果表明,光程放大因子还受滤膜 颗粒物富集量的影响. 因此,对于不同水体,悬浮颗 粒物吸收系数测量需要采用不同光程放大因子,一般 来说滤膜富集量可通过过水体积来控制,具体表现在 样品测量的吸光度上,根据 Tassan 等[10]的结果,T-R 法光程放大因子在样品吸光度值介于 0.1~0.5 时比 较稳定,在不同的吸光度范围应采用不同的光程放大 因子经验参数;而对于吸收法,Röttgers等[18]给出的 最佳吸光度范围为 0.02~0.1,对于 0.1 < D < 0.5 的 样品可通过二次多项式进行计算,不建议测量 D> 0.5 的样品. 即使如此,这些已公布的光程放大因子 的值和经验参数都是平均值,应用在不同水体上还是 有一定差异. 实际操作中建议按照前文推荐的吸光 度范围进行样品过滤以减小计算误差,在条件允许的 情况下,建议对研究水域的水体进行光程放大因子测 量,取其平均值作为以后测量和计算悬浮颗粒物吸收 系数时的光程放大因子.

2.6 各影响因素的误差分析

前文主要研究了影响悬浮颗粒物吸收系数测量 结果的各种因素,如滤膜差异性、滤膜含水量、滤 膜颗粒物分布不均匀、过水体积以及光程放大因子 等,这些因素最终会导致吸收系数的测量存在误差. 本节主要分析各影响因素对吸收系数测量结果的影 响并进行误差计算. 研究中各影响因素对吸收系数 测量结果造成误差的计算方法如下:对于滤膜差异 性,计算60~120 min 各空白样品滤膜光学密度的 标准偏差与该样品吸光度的比值作为其对测量结果 的误差:对于滤膜含水量,计算不同时刻(含水量) 样品的吸光度与样品平均吸光度的误差作为其对测 量结果的误差;对于颗粒物均匀性,误差计算方法 参照2.3节;对于过滤体积,计算各体积下吸收系 数与颗粒物平均吸收系数之间误差作为其对测量结 果的误差. 至于光程放大因子对测量结果的影响, 文中使用线性拟合的平均光程放大因子计算每个样 品的吸收系数,并计算其与真实吸收之间的误差,误 差 σ 计算公式为:

$$\sigma = \frac{a_{\rm m} - a_{\rm AC-s}}{a_{\rm AC}} \times 100\% \tag{3}$$

式中, a_m 为采用文中得出的光程放大因子计算的吸收系数, a_{AC-s} 为真实吸收系数. 将计算的各影响因素对吸收系数测量结果的误差求平均值并以表格形

式给出,考虑到遥感应用,本研究以440和550 nm 处的平均相对误差为例,见表4.

表 4 各影响因素在 440 和 550 nm 波长处对吸收系数测量结果造成的平均相对误差/%

Table 4 Mean relative error of absorption coefficient at wavelengths of 440 nm and 550 nm caused by differen	ifferent influence factors/%
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影响因素	A法(440 nm)	A 法(550 nm)	T-R 法(440 nm)	T-R 法(550 nm)	T法(440 nm)	T法(550 nm)
滤膜差异性	0. 11	0. 24	_	_	2. 19	5. 17
滤膜含水量	2. 72	3. 18	_	_	0.89	1.01
颗粒物分布均匀性	7. 81	5. 97	28. 73	30. 54	26. 67	32.72
过滤体积	9. 02	6. 05	11.02	6. 18	13. 10	10. 29
光程放大因子	12. 13	12. 11	16. 13	15. 74	23. 59	21. 89

1)"一"表示文中没有数据

从表 4 可看出,各影响因素对吸收系数的测量结果都有一定的影响,影响程度不一.对比各个因素造成的误差可发现,空白滤膜差异性及滤膜含水量对测量结果的影响较小;颗粒物分布均匀性与过滤体积对测量结果有较大影响;光程放大因子是测量结果最大的误差来源,以440 nm 波长处误差为例,A 法测量平均相对误差达12.13%,T 法和T-R 法测量平均相对误差达23.59%和16.13%.总体来看,A 法测量结果受各个影响因素的影响程度较T 法和T-R 法低,与前文分析的结果一致,因此条件允许的情况下,采用 A 法进行颗粒物吸收系数的测量能降低受这些因素导致的测量误差.

3 结论

- (1) A 法测量结果与 T 法和 T-R 法的相比,受空白滤膜差异性和滤膜分布是否均匀等因素的影响小,测量精度较高.
- (2) 同一样品在相同条件下, A 法测量结果分别与 T 法和 T-R 法有良好的线性关系, 相关系数分别为 0.94 和 0.99, 3 种测量方法得出的数据可比.
- (3) 光程放大因子的实验表明,光程放大因子随着过滤体积的增大而减小. A 法、T 法和 T-R 法通过线性拟合获取的光程放大因子的平均值分别为 4.01、2.32 和 2.20,相关系数分别为 0.90、0.80 和 0.87,光程放大因子为常数. 采用波长吸光度依赖的二次多项式拟合的方法提高了测量精度,相关系数分别提高为 0.95 和 0.94. A 法测量的结果优于 T-R 法的结果,多项式拟合优于线性拟合.
- (4)分析各影响因素对测量结果造成的误差可发现,光程放大因子是吸收系数测量结果最大的误差来源,以440 nm 波长处误差为例,采用 A 法、T 法和 T-R 法测量的平均相对误差分别为12.13%、23.59%和16.13%.

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