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元素与稳定同位素微化学分析在水产品产地溯源中的应用*

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摘要 随着人们对水产品需求的快速增长,消费者对水产品原产地信息也越来越重视。鉴于以假充真、以次充好的不法行为严重影响消费者和生产者的合法权益,开发更有效的水产品溯源、真伪鉴别及原产地保护体系愈发重要。与此相适应,本文重点综述了基于矿质元素与稳定同位素地理“指纹”溯源技术的基本原理及其在水产品产地溯源中的研究进展,以期为今后相关技术的开发提供理论依据。

关键词 矿质元素; 稳定同位素; 水产品; 产地溯源; 微化学

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水产品是海洋和淡水渔业生产的动植物及其加工产品的统称,常见的水产品主要包括鱼、虾、蟹和贝。水产品富含蛋白质、维生素和矿质元素(姜晓东等, 2015; 赵亭亭等, 2018),具有极高的营养价值,其需求量逐年提高,传统捕捞的数量已完全无法满足消费者的需求,相关名特优新品种的养殖业也得到迅猛发展和高度关注。需要注意的是,随着消费者对水产品品质的追求及对知名产地或著名品牌水产品更加青睐,优质水产品,如阳澄湖中华绒螯蟹(*Eriocheir sinensis*)、波士顿龙虾(*Homarus americanus*)等可以售出更高的价格。鉴于此,不法商人常以假充真、以次充好来赚取非法利益。目前,除掺假行为外,原产地标识不清(Miller *et al.*, 2010; Lamendin *et al.*, 2015)及

错贴标签(Wallstrom *et al.*, 2020)的现象也大量存在。这种恶意行为必会损害消费者、生产者及行业的利益。

为使消费者合法权益得到保障,欧盟 2065/2001号规定要求水产品标签必须注明水产品的获取方法(养殖或野生)、养殖国家与产地的地理位置等信息,但我国尚无如此严格的要求。养殖水产品冒充野生水产品以及普通产地水产品假冒知名地理标志保护产地水产品的现象频发,严重危害着原产地水产品的信誉和消费者的正当权益。在这种市场背景下,亟需进一步加快和强化对水产品的原产地溯源研究,以便建立更多、更有效且更为科学、客观的方法体系对水产品所标识的产地进行有效监督、鉴定,从而确保其产

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地或品牌来源信息真实。

矿质元素和稳定同位素分析是目前两类水产品产地溯源最受关注的方法(陈胜军等, 2019; 张政权等, 2020)。本文对矿质元素、稳定同位素指纹及其相关的多元统计分析技术在水产品溯源中的原理与应用进行综述与展望, 以期为名特优新水产品产地溯源技术的发展提供思路。

1 元素微化学分析与水产品产地溯源

1.1 元素微化学溯源的技术原理

矿质元素在生态环境中的分布很不均匀。不同的水、土壤、饲料和空气环境中的矿质元素组成和

含量都有其各自的特征(Franke *et al*, 2005), 且不同生境条件中的常量、微量元素会因为多种生命活动而进入动植物体内持续累积, 导致来源于不同地区的生物体内元素含量存在较大差异(Anderson *et al*, 2005), 故这种微化学“指纹”的差异可以成为很好的产地溯源指标(图 1)。基于该原理, 如果对经济水产品中的元素含量和组成“指纹”进行精准定量检测, 可以达到相关水产品产地溯源的目的。虽然由于饲料中常添加一些必需元素, 水产品的某些矿质元素含量也有可能受到饲料的影响, 但如果挑选饲料影响小的稳定元素, 且对尽量多种的元素进行综合分析, 则在进行产地判别时, 可以有效避免受到人为因素(如污染、饵料等特殊情况)的干扰。

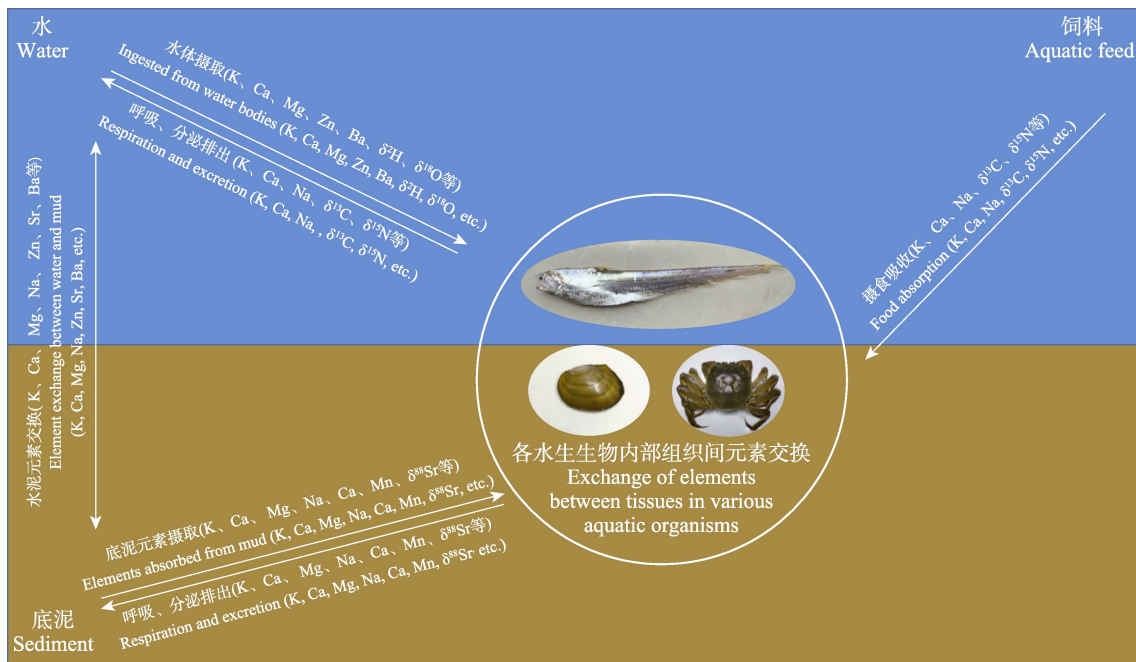


图 1 微化学“指纹”溯源原理模式

Fig. 1 Schematic diagram of the traceability by microchemical “fingerprint” profiles

1.2 水产品产地溯源中的元素微化学分析进展

在水产品的产地溯源应用中, 鱼类应用最为广泛, 因为鱼类在水体中生活的过程中, 其耳石结构会持续地吸收水环境中的矿质元素并且不断富集(Campana *et al*, 2007)。耳石中的 Sr 与 Ba 元素的主要来源就是生活的水环境, 因此, 通过测定耳石的元素进行产地溯源是一种重要方式(Kerr *et al*, 2014)。Avigliano 等(2017)运用电感耦合等离子体发射光谱仪(ICP-OES)对拉普拉塔河 3 个不同地区的条纹鲮脂鲤(*Prochilodus lineatus*)耳石的 Sr、Ba、Zn 与 Ca 元素的比值进行了测定, 在后续的判别分析中, 3 个产

地的判别准确率分别为 82.1%、84.2%和 77.8%, 虽然将元素与几何形态学方法结合的判别更为准确, 但单独使用元素指纹判别的准确率要明显优于只使用几何形态学方法。Miyani 等(2016)通过电感耦合等离子体发射光谱仪(ICP-AES)测定了来自恒河及其支流的 4 个不同产地的胡子鲶(*Clarias batrachus*)矢耳石的 Na、Mg、Ba 和 Cu 等 12 种矿质元素的含量, 结果显示, 在 4 个不同产地中, 除 Na、Ca 和 Sr 元素外, 其余 9 种元素均存在显著性差异, 通过 12 种元素对 4 个产地的判别分析准确率分别为 88%、92%、96%和 100%, 总体的准确率达 94%, 产地判别效果非常好。该研究还对同样 4 个产地的样本进行几何形态学

方法的产地判别, 产地判别准确率仅为 68.39%, 与 Avigliano 等(2017)的研究结果相同, 均表明矿质元素的判别效果显著优于几何形态学方法。耳石矿质元素含量同样被 Maciel 等(2020)应用于大西洋西南部 4 个河口的叉尾髯海鲉(*Genidens genidens*)的群体判别, 电感耦合等离子体质谱仪(ICP-MS)和激光剥蚀电感耦合等离子体质谱仪(LA-ICP-MS)被用于测定耳石边缘与核心部分 Ba、Cu 和 Mg 等 7 种矿质元素与 Ca 的比值; 边缘部分的综合判别率为 75.9%, 核心部分的综合判别率为 86.2%, 对群体的判别效果较好; 通过耳石的几何形态学方法对 4 个群体判别的准确率为 75.1%, 低于矿质元素的判别效果。通过肌肉对不同地区鱼类的判别效果同样优异, Han 等(2019)采集了中国 2 个不同地区同一年 4 个季节的鲑鱼(*Oncorhynchus keta*)样本, 通过 18 种矿质元素的测定不仅可以将 2 个不同产地的鲑鱼进行产地鉴别, 也进一步验证了多元素的产地溯源技术在对鲑鱼产地的鉴别中不会受到季节影响, 证实了该技术的应用价值。

近年来, 矿质元素分析也越来越多地应用在虾、蟹和贝类的研究中。杨文斌等(2012)通过 ICP-MS 测定了中华绒螯蟹第 3 步足的 Na、Mg、Al 等 11 种矿质元素的含量, 对长江水系 3 个不同湖泊产的中华绒螯蟹进行产地判别的准确率达到 93.3%。杨健等(2013)同样基于第 3 步足整体组织进行测定, 选取 Na、Mg 等 12 种测得的矿质元素对相距较近的 3 个湖泊及距离较远的军山湖中华绒螯蟹进行产地判别, 对 4 个产地的判别准确率达 100%。赵鉴等(2014)分别选取辽河水系以及长江水系的 4 个不同产地, 基于第 3 步足内 Na、Mg 等 12 种矿质元素进行产地判别, 对 4 个产地的判别准确率同样可达 100%。Varrà 等(2021)使用四极感应耦合等离子体质谱仪(Q-ICP-MS)测定了地中海和大西洋 3 个不同地区的 68 尾普通乌贼(*Sepia officinalis*)样本的 52 种元素含量, 主成分分析后选用了 3 种不同的判别分析方法对这 3 个产地的普通乌贼进行产地判别, 3 种方法的交叉验证判别准确率分别为 100%、99%和 100%, 可以准确地对不同来源乌贼进行区分。

在贝类研究中, Zhao 等(2016)对采集于中国 3 个省份海岸的菲律宾蛤仔(*Ruditapes philippinarum*)进行产地判别, 采用 ICP-MS 测定蛤仔软组织及同步采集的生活水样与泥样的 25 种矿质元素的含量, 3 个产地的总体判别准确率为 94.4%, 具有较好的产地判别效果; 相关性分析的结果显示, Na、Mg、Co、Cu 等 12 种元素在蛤仔与水泥间存在显著相关性, 有效

证实水生生物体内的矿质元素会因为生活水体环境的变化而变化。Bennion 等(2019)使用 ICP-MS 测定采集于爱尔兰西海岸 3 个海湾的 4 个不同产地的贻贝(*Mytilus edulis*)的 As、Cd 等 9 种元素, 并进行产地判别, 发现不同组织有不同的判别效果; 但将清洁的贝壳、足部和角质层相结合之后, 对 4 个不同地区(其中有 2 处采样地点的间距仅为 6 km)的贻贝判别准确率可达到 100%。Morrison 等(2019)通过 ICP-MS 对采集于爱尔兰西海岸 3 个海湾共 4 个不同地点的扇贝(*Pecten maximus*)进行了产地的判别。其基于 10 种矿质元素、选取贝壳及软组织分别进行了矿质元素的产地判别研究。结果显示, 贝壳的判别达到 97.5%的判别准确率, 具有满意的产地溯源效果。将软组织与贝壳数据相结合之后可进一步提高判别率至 100%。Forleo 等(2021)共采集了 7 个地区 25 个采样点的紫贻贝(*Mytilus galloprovincialis*)进行产地溯源研究, 通过 14 种矿质元素的测定及分析, 总体的产地溯源准确率达 90%以上, 可以有效应对市场上的假冒行为。Ricardo 等(2020)利用矿质元素快速、准确、有效地进行了花蛤(*Ruditapes philippinarum*)的产地溯源。

矿质元素不仅被应用于不同产地的水产品的产地鉴别之中, 也可以用于对不同养殖方式水产品的鉴别, 可以极好地保护野生名贵水产品的信誉。Anderson 等(2010)利用 19 种元素建立了 5 种不同的模型, 尝试对 2 种生长方式(养殖与野生)的鲑[大西洋鲑(*Salmo salar*), 大鳞大马哈鱼(*Oncorhynchus tshawytscha*)和银大麻哈鱼(*Oncorhynchus kisutch*)]进行区分, 虽然根据不同的模型, 准确度略有不同, 但能够成功地把不同产地与生产方法的鲑鱼区分开来。Zitek 等(2010)使用激光剥蚀电感耦合等离子体质谱仪(LA-ICP-MS)对野生与人工养殖的鳟(*Oncorhynchus mykiss*和*Salmo trutta*)的耳石进行元素测定, 基于 $^{88}\text{Sr}/^{43}\text{Ca}$ 和 $^{23}\text{Na}/^{43}\text{Ca}$ 等分析, 可以 100%区分野生与养殖的鳟。Li 等(2015)通过 ICP-AES 对不同养殖模式的斑点叉尾鲴(*Ictalurus punctatus*)进行肌肉矿质元素的比较研究, 结果显示, 用 13 种矿质元素“指纹”判别不投与投喂饲料养殖斑点叉尾鲴的准确率可达 100%。

随着矿质元素“指纹”的研究种类与范围的不断扩大, 矿质元素“指纹”的应用前景必会更加广阔, 但我国目前特色水产品的产地溯源研究仍处于初始阶段, 还有很多特色水产品缺乏相关特征指标的研究, 特色水产品的元素“指纹”图谱的建立仍然需要更多的样本量以及更多产地的数据支持。

2 稳定同位素微化学分析与水产品产地溯源

2.1 稳定同位素微化学“指纹”溯源的技术原理

质子数相同、中子数不同的同一元素的不同核素被称为同位素,水产品体内某元素的比值受同位素分馏效应的影响。同位素分馏效应是指由于同位素质量不同,在物理、化学及生物化学作用过程中,同位素比值不同的两种物质或同种物质的两种相态间发生的同位素的自然分配效应(Nier, 1950)。同位素分馏效应受气候、环境、生物代谢等因素影响而存在差异(Branch *et al.*, 2003; Liu *et al.*, 2017)。同位素的波动范围相对较小,相对稳定,如同人类的指纹具有各自的特征信息,被称为“同位素指纹”。稳定同位素比质谱仪(IRMS)技术具有精确度高、运用少量样品即可进行同位素检测和区分,且没有放射性,不会造成二次污染的优点。该技术在草莓(Perini *et al.*, 2017)等植物源性水果和牛羊肉(Zhao *et al.*, 2015)等动物源性肉品中均得到了运用。近年来,在水产品溯源中也有了类似的应用(Pereira *et al.*, 2019),特别是 $\delta^{13}\text{C}$ 、 $\delta^{15}\text{N}$ 、 $\delta^2\text{H}$ 和 $\delta^{18}\text{O}$ 等。

水产品体内的 C 稳定同位素组成与饲料的种类密切相关。 $\delta^{13}\text{C}$ 会因为动物饲料中 C_3 、 C_4 植物比例的不同而发生变化。 $\delta^{15}\text{N}$ 除受饲料内动植物占比的影响外,还受到土壤状况等多种因素的影响(Amundson *et al.*, 2003)。水体中的 $\delta^2\text{H}$ 、 $\delta^{18}\text{O}$ 值会受到不同季节、海拔与生存纬度的影响而产生变化,因此,生活在不同水环境中的水产品的 $\delta^2\text{H}$ 、 $\delta^{18}\text{O}$ 值会有较大的差异(周毅等, 2017; Ramesh *et al.*, 1992),也极具产地溯源的潜力。另外, Sr 稳定同位素受到地质条件的影响较大,比 H、O 稳定同位素比值更稳定,可在 H、O 稳定同位素无法进行有效区分的水产品中进行溯源研究(Kelly *et al.*, 2005)。

2.2 水产品产地溯源中的稳定同位素微化学分析进展

稳定同位素技术已经越来越多地应用到鱼类的产地溯源研究。Kim 等(2015)选取了 11 个不同产地的鲭(*Scomber japonicas*)、6 个产地的小黄鱼(*Larimichthys polyactis*)及 7 个产地的鳕(*Theragra chalcogramma*)的肌肉组织,进行 C、N 稳定同位素的测定,结果显示,鲭与鳕的产地地区分度很高,但小黄鱼的区分度极不理想。吴浩等(2021)对来自于 6 个不同国家的大西洋鲑进行产地溯源研究,选取三文鱼的肌肉、表皮、鳞片和骨骼测定了 C、N、H、O 和 S 稳定同位素比值,结果发现,表皮、鳞片和骨骼的 C、

N 与 S 同位素产地判别准确率均达 100%。在 Molkontin 等(2015)的研究中,通过 C、N 同位素还可以将野生鲑与养殖鲑进行准确区分,即使鲑鱼肉在烟熏后仍然可以准确的产地溯源。

除鱼类外,同位素溯源技术在贝、海参和虾蟹类的产地溯源中同样广受关注。Zhang 等(2019)分别在同一年春季和秋季采集了中国黄海与渤海海域 7 个地点的虾夷扇贝等 3 种扇贝(*Patinopecten yessoensis*, *Chlamys farreri* 和 *Argopecten irradians*)进行了肌肉 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 测定,判别结果显示,对所采集的 7 个地点的扇贝的综合判别准确率达 92%。Zhao 等(2019)分别在不同季节采集了中国海域 6 个不同地点的虾夷扇贝,对所有样本的 10 种氨基酸进行了 C、N 同位素比值的测定,产地判别正确率亦可达 100%。 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 还被应用在了茎柔鱼(*Dosidicus gigas*)的产地溯源研究中。Gong 等(2018)与 Liu 等(2019)均采集了东太平洋不同地区的茎柔鱼进行产地溯源研究,通过 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 均达到了较好的产地溯源效果。后者的研究还证明了部分地区的茎柔鱼存在可能的种群关联性。Liu 等(2017)对海参(*Apostichopus japonicus*)测定了特定脂肪酸内的 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 值,对采集于不同季节和不同地点的海参样本进行溯源。除长海岛与獐子岛的区分度可能因地理接近或食物相近而区分度不高外,其余产地的判别结果均可达 79.0%。Li 等(2018)采集了中国 16 个地区的凡纳滨对虾(*Litopenaeus vannamei*)测定 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 值,低盐度、高盐度与淡水产地虾的整体判别准确率为 89.6%;研究还发现, $\delta^{13}\text{C}$ 值主要是因为咸水内的富集产生差异,而 $\delta^{15}\text{N}$ 的差异主要是来源于饲料。Yin 等(2020)则利用多接收器电感耦合等离子体质谱(MC-ICP-MS)测定了步足及背甲等组织中 Sr 稳定同位素比($^{87}\text{Sr}/^{86}\text{Sr}$),尝试进行我国 5 个不同的产地中华绒螯蟹的溯源研究,结果显示,相同湖区的螃蟹与水样 Sr 稳定同位素比值相近,但不同湖区的值则存在显著差异,可进行产地溯源。结果也证实了 Sr 稳定同位素比值主要受水体环境而非饲料的影响。

稳定同位素溯源技术不仅可以对水产品进行产地鉴别,也可用来区分不同养殖方式的水产品。Camin 等(2018)对 20 个意大利养殖场的 130 条意大利虹鳟进行鱼肉的 H、C、O、N 和 S 同位素分析,综合判别使用不同饲料养殖场虹鳟的准确率达 91%;鱼体 C、N 和 S 同位素比值与饲料的比值呈正相关,而鱼体 H 和 O 同位素比值则与水体的比值呈正相关。Wang 等(2018)对野生及不同养殖(传统养殖、有机养殖)条件

的鲑进行溯源发现, C、N 稳定同位素比值可精准确定上述 3 类养殖方式。Tulli 等(2020)也通过 C、N、H 和 O 同位素区分了不同地区及不同养殖系统的欧洲鲑鱼(*Dicentrarchus labrax*)。

虽然稳定同位素技术在产地溯源中的应用已经取得了许多成功, 但目前的研究深度仍然不足, 许多研究仍局限于较少的产地范围及样本数量, 在后续的相关研究中, 对采样地区与样本数量需进一步扩大, 以建立完整的同位素“指纹”数据库。

3 矿质元素和稳定同位素结合分析用于水产品产地的溯源

3.1 矿质元素和稳定同位素结合分析的技术原理

不同环境条件下的常量、微量矿质元素会因为摄食、呼吸等生命活动在水生动物体内持续累积, 导致来源于不同地区的水生动物体内元素含量会存在较大差异。对于同位素指标而言, 水产品体内的 C、N 稳定同位素组成受到水生动物所食用饲料的密切影响; H、O 同位素组成会因为水体环境的差异而形成产地上的较大的差异(Ramesh *et al*, 1992); Sr 稳定同位素则受到地质条件的影响较大。不同的溯源指标因为影响因子的不同在进行产地溯源研究时会有极好的互相补充的效果, 因此在进行产地溯源时, 越来越多的研究将多种指标进行综合分析以取得比选取单一因素更好的溯源效果。

3.2 水产品产地溯源中的矿质元素和稳定同位素结合分析进展

元素指纹和同位素指纹技术均在水产上具有广泛的应用潜力, 而这 2 种技术的综合利用具有更好的产地溯源效果。2000 年以来, 将同位素比值和多元素分析相结合进行水产品产地溯源的研究不断增多。黄丽英等(2019)测定了 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 以及 Na 等 10 种矿质元素的含量以区别不同渔场产带鱼(*Trichiurus haumela*)。虽然 4 个渔场间的 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 值无显著差异, 但将稳定同位素比值与矿质元素含量相结合后进行的主成分分析中, 成功区分 4 个渔场的带鱼, 且相互没有重叠。Luo 等(2019)在区分长江水系 8 个不同产地中华绒螯蟹时, 仅使用 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 值时判别准确率为 82.3%, 仅使用矿质元素的判别准确率为 91.5%, 将二者结合之后的判别准确率可达 98.2%, 判别效果有显著提升。骆仁军等(2020)在对东营、盘锦、营口 3 个地区的中华绒螯蟹的产地鉴别中发现, 以 $\delta^{13}\text{C}$ 和 $\delta^{15}\text{N}$ 值为溯源指标进行产地鉴别, 其原始

正确率仅为 66.7%, 交叉判定正确率为 65%, 而利用多元分析方法结合稳定同位素和元素组成时, 其产地溯源初始正确率高达 96.7%, 交叉判定正确率为 91.7%。在对海参的产地溯源研究中, Kang 等(2021)将 C、N、O 和 H 同位素比值与 22 种矿质元素含量相结合, 对我国 5 个不同产地的海参进行溯源研究发现, 判别分析的准确度可在 96%以上。Liu 等(2020)将鱼鳞的微量元素与 C、N 同位素比值结合, 对野生、湖养和池养的鲤鱼(Cyprindae)进行产地区分, 训练集的判别准确率高达 100%。

在国外的相关研究中, Carter 等(2015)对澳大利亚本地与亚洲邻国进口的斑节对虾(*Penaeus monodon*)等虾类的壳、几丁质及肌肉进行微量元素与同位素分析, 结果显示, 进口对虾与澳大利亚对虾等存在显著差异。同时, 肌肉与几丁质间的同位素组成存在较强的相关性, 表明可以从这 2 个成分中得到等价信息, 只需要对其中 1 个进行分析即可得到产地结果。Ortea 等(2015)将元素与同位素分析相结合, 采集了 3 个属的 7 种对虾[斑节对虾、凡纳滨对虾、印度明对虾(*Fenneropenaeus indicus*)、墨吉明对虾(*Fenneropenaeus merguensis*)、红对虾(*Farfantepenaeus notialis*)、阿根廷红虾(*Pleoticus muelleri*)和北极虾(*Pandalus borealis*)], 将两种技术结合后成功地区分了不同种类、不同起源的对虾, 同时还成功区分出野生与养殖虾。

稳定同位素技术与多矿质元素分析相联用, 并与多种化学计量学分析方法相结合是产地溯源的研究热点。将矿质元素与同位素相结合进行产地溯源的研究, 比使用单一方法具有更高的判别准确率。

4 结论

近年来, 矿质元素与稳定同位素技术在鱼类、甲壳类和贝类水产品的产地成功溯源的应用越来越多。随着人民对美好生活的需求日益增长、对水产品质量安全的问题更加关注, 且随着现代渔业提质增效和绿色转型步伐的加速和乡村振兴国策的实施, 水产品产地溯源和品牌保护机制将会得到进一步的健全。除矿质元素与稳定同位素技术外, 形态学方法、分子生物学技术与仿生感官评价技术等产地溯源中均有成功应用。综合利用更多元素和同位素微化学“指纹”以及在此基础上结合更多具有产地差异性的指标来开发更有效的技术应该是今后产地溯源研究的趋势, 同时, 建立从地区到国家层面的水产品产地溯源和原产地保护大数据库的工作同样需要得到高度重视。

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Progress in Multi-Element and Stable Isotope Analysis for Geographical Origin Traceability of Aquatic Products

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Abstract Aquatic products are a general term referring to marine and freshwater fishery organisms and their products. Such products mainly include fish, shrimp, crabs, shellfish, and seaweed. Aquatic products are rich in nutrients such as proteins, vitamins, fatty acids, and minerals. However, the recent illegal counterfeiting of the geographic origin label for aquatic products has become a major problem, receiving increasing attention worldwide. China is the largest producer of aquatic products globally, with a wide variety of aquatic species (especially fish, shrimp, crab, shellfish, sea cucumber, and microalgae). Several of these products are famous, exotic, high-quality, and new or endorsed by protected designations of origin. As an increasing number of consumers pursue better quality aquatic products, many well-known aquatic product brands and the protection of geographical indication products have been established. Consumers prefer aquatic products of well-known origins or famous brands, and are willing to pay higher prices for their quality. It is noteworthy that unscrupulous businessmen frequently fake shoddy products as real ones to earn profits. In addition to adulteration, the unclear origin identification and mislabeling are also rampant. Counterfeit activities inevitably harm the legitimate interests of consumers, producers, and the fishery industry. Using “bathed” Chinese mitten crab to counterfeit the native crabs cultured in the Yangcheng Lake of Jiangsu Province is a typical case of the above-mentioned activities. However, the establishment of traceability systems related to aquatic products remains unaccomplished in China. Thus, it is imperative to accelerate research on the origin traceability of aquatic products, and use scientific and objective methods to identify and confirm the origin of the products. Moreover, accurate and reliable analysis approaches are a prerequisite for effectively solving the adulteration and mislabeling of aquatic products and have special significance for implementing the national policy of rural revitalization. So far, biogeochemical approaches have especially advanced with a set of techniques for traceability of aquatic product origins. In particular, the corresponding mineral elements (e.g., Sr, Ba, Zn, Ca, Na, Cu, Mg, Al,

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As, Be, Co, Cr, Fe, K, Mn, Ni, P, Ti, and Zn) and stable isotopes (e.g., $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$) analyses have received increasing attention. The composition and content of mineral elements and ratios of stable isotopes in different habitats of aquatic organisms have individual characteristics and the mineral element/stable isotope “fingerprints” profiles in aquatic products must be different owing to various bioassimilation and bioaccumulation processes of the elements to the organisms from different geographical production regions of either natural or aquaculture water environments. Therefore, chemometric (especially, multivariate statistical authenticity analysis, e.g., discriminant analysis and principal component analysis) models based on the aforementioned “fingerprints” profiles (i.e., multi-elements, multi-stable isotopes, and the combination of multi-element and stable isotope) can be used to discriminate between aquatic products of wild or farmed origin, geographical origin, and species authenticity. This review summarizes the progress of the principles and applications of approaches to multi-mineral elements and stable isotopes traceability in aquatic products. Although the element uptake in fishery organisms may be influenced to some degree by water pollution and artificial diet, the availability of multi-elements/stable isotopes in ambient habitat waters and their bioassimilation/bioaccumulation are the most consistent and prominent factors influencing the biogeochemical “fingerprint” profiles in aquatic products. Advanced chemical analysis techniques can precisely and accurately reveal these profiles; for example, inductively coupled plasma (ICP) optical emission spectroscopy, ICP-atomic emission spectroscopy (ICP-AES), ICP-mass spectrometry (ICP-MS), laser ablation-ICP-MS, single collector quadrupole-ICP-MS, isotope ratio mass spectrometry, and multi-collector-ICP-MS. Successful studies of geographical origin traceability have already been reported in literature involving in many fishery species; e.g., *Prochilodus lineatus*, *Genidens genidens*, *Eriocheir sinensis*, *Sepia officinalis*, *Dosidicus gigas*, *Ruditapes philippinarum*, *Mytilus edulis*, *Mytilus galloprovincialis*, *Patinopecten yessoensis*, *Chlamys farreri*, *Argopecten irradians*, *Pecten maximus*, *Salmo salar*, *Oncorhynchus mykiss*, *Salmo trutta*, *Oncorhynchus tshawytscha*, *Oncorhynchus kisutch*, *Ictalurus punctatus*, *Scomber japonicus*, *Larimichthys polyactis*, *Theragra chalcogramma*, *Apostichopus japonicus*, *Litopenaeus vannamei*, *Dicentrarchus labrax*, *Trichiurus haumela*, tiger prawns, and several Cyprinidae species. The present article provides the most recent references and important theoretical bases for the development of more effective traceability and authenticity detection technologies for the famous, special, high-quality, and new aquatic products, promoting the implementation of national policies for rural revitalization. In addition, the establishment of local and national level databases is strongly suggested for effective geographical origin traceability of aquatic products in China.

Key words Multi-elements; Stable isotopes; Aquatic products; Geographical origin traceability; Microchemistry