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Relating Water and Otolith Chemistry in Chesapeake Bay, and Their Potential to Identify Essential Seagrass Habitats for Juveniles of an Estuarine-Dependent Fish, Spotted Seatrout (*Cynoscion nebulosus*)

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ABSTRACT

RELATING WATER AND OTOLITH CHEMISTRY IN CHESAPEAKE BAY, AND THEIR POTENTIAL TO IDENTIFY ESSENTIAL SEAGRASS HABITATS FOR JUVENILES OF AN ESTUARINE-DEPENDENT FISH, SPOTTED SEATROUT (*CYNOSCION NEBULOSUS*)

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A quantitative understanding of habitat use of estuarine-dependent fishes is critical to the conservation of their most essential habitats. Because recruitment and fitness may be influenced by the quality of juvenile habitats, developing methods to quantify habitat-specific survivorship is pivotal to such understanding. An initial step to quantify survivorship is to validate the habitat-specific natural tags contained in otoliths. To this aim I investigated the variability in the chemistry of surface waters and otoliths of juvenile spotted seatrout, *Cynoscion nebulosus*, in five seagrass habitats of Chesapeake Bay, namely: Potomac, Rappahannock, York, Island, and Eastern Shore. I measured Mg, Ca, Mn, Sr, Ba, and La in water and otoliths by inductively coupled plasma-mass spectrometry, and $\delta^{13}C$ and $\delta^{18}O$ in otoliths using an automated carbonate analyzer. Multivariate analyses of variance and regressions were used to test the hypothesis that otoliths accurately record the chemistry of natal habitats of juveniles, whereas cross-validated *k*-nearest neighbor functions were derived to discriminate habitats based on water and otolith chemistry. Concentration of Mg, Mn, Sr, and Ba in water was significantly different between habitats independent of temporal variation. Classification accuracy of water samples was low in Rappahannock (37%), moderate in Potomac and Eastern Shore (60-70%), and high in York and Island (81-82%) habitats. Weighted

regressions showed that salinity could predict accurately $[Ba/Ca]_{otolith}$ and $[La/Ca]_{otolith}$. There was a positive correlation between $[Ba/Ca]_{otolith}$ and $[Ba/Ca]_{water}$, but the relation was not linear as previously found in laboratory experiments. Contrary to expectation, $[Sr/Ca]_{otolith}$ did not correlate with water chemistry, however there was a predictive relation between $[\delta^{18}O]_{otolith}$ and $[Sr/Ca]_{water}$. Otolith microchemistry of juveniles collected in 1998 and 2001 was significantly different among habitats within and between years, but the ability of trace elements to allocate individual fish to natal habitats was variable (0-82%). However, the combination of [Ba/Ca], [Mn/Ca], with $\delta^{13}C$ and $\delta^{18}O$ in 2001 otoliths significantly improved classification rates, allowing 82-100% accuracy. These results showed that otolith microchemistry might be useful in identifying specific seagrass beds in Chesapeake Bay, with the potential of being used as natural tag to quantify survivorship and to determine essential habitats for juvenile spotted seatrout.

Dedicated to

my wife, Laura M. Dorval, for her love and for gracefully

sharing the burdens of graduate school with me.

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CHAPTER I

GENERAL INTRODUCTION

1.1. Ecological context

Understanding the spatial ecology of marine and estuarine fish populations is fundamental to their sustainable exploitation and conservation, because the structure of physical factors in space may influence populations in the same magnitude as vital rates, competition, and predation (Hanski 1998). Physical factors, acting on different life stages, affect the spatial distribution of populations, while determining their stability and persistence through time (Botsford et al. 1994; Alexander and Roughgarden 1996). Large-scale physical processes, such as currents and fronts, have historically played an important role in the reproductive isolation of groups of fish, resulting in genetically different populations (Sinclair and Iles 1981; Sinclair 1988; Gold and Richardson 1998a, 1998b; Gold et al. 1999). Small-scale variations in the flow, temperature, and salt distribution within an estuary may affect the dynamics of genetically homogeneous populations leading to strong spatial structure among groups of fish (Baker et al. 1986; Baker and Matlock 1993), and potentially to divergent life history strategies within populations (Secor 1999; Secor et al. 2001).

At all scales, biogeochemical processes are coupled to the physical environment, influencing spatial variation in habitat quality for fish populations. Geochemical and physical processes interact to regulate the concentration and the distribution of elements and nutrients in aquatic systems. Such interaction is best manifested in areas of steep temperature and/or salinity gradients, such as fronts. Fronts are areas of high primary and

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The journal model is taken from Canadian Journal of Fisheries and Aquatic Sciences.

secondary productivity that are generally associated with high aggregations of fishes (Legett et al. 1977). Fronts are also transition areas between different water masses, where intense biogeochemical reactions take place. As an example, in the estuarine mixing zone increased salinity causes flocculation of river colloids and fractionation of trace elements (Sholkovitz 1978; Powell et al. 1996; Wen et al. 1999). In addition, fronts may act as physical barriers that control the exchange of trace and minor elements between different water masses (Shumilin et al. 1993). Likewise, the variability in physical and biogeochemical properties of waters determine habitat quality for fish populations, and may influence major life-history events such as the timing of feeding and spawning migrations (Legett 1977; Harden-Jones 1982).

The effect of these spatial processes on the life history of fish populations is receiving sustained interest in fishery ecology because of continuing overexploitation of most stocks (i.e., unit populations) and the degradation of essential-fish habitat. Fishing has altered the life-history traits (e.g., growth rate, age-at-maturation) of many fish populations (Law 2000), destabilized competitive interaction among others, while decreasing the population's ability to respond to environmental change (Hughes 1994; Bladder et al. 2000; Law 2000). Habitat degradation may decrease foraging, shelter, and nursery areas of fishes, affecting their fecundity, growth, and survivorship (Hughes 1994; Rooker et al. 1998; Cattrijsse et al. 2002). Likewise, the negative effect of both fishing and habitat degradation has contributed to the extirpation of many fish stocks, while threatening the persistence of many others (e.g., Hughes 1994; Hutchings and Myers 1994; Bladder et al. 2000).

Estuarine fishes are among the most threatened organisms by fishing and habitat degradation. Estuarine habitats, such as seagrasses, are one of the most productive areas in coastal ecosystems (Nybbaken 1997), and are primary nurseries for juvenile fish (Bell and Pollard 1989; Sogard and Able 1991; Hannan and Williams 1998). However, these habitats have declined worldwide because of eutrophication (Orth and Moore 1983; Short and Burdick 1996), diseases (Short et al. 1986), physical disturbance (Giesen et al. 1990), and land-use (Cattrijsse et al. 2002) among other causes. Because world estuaries have historically supported important commercial and recreational fisheries, the loss of estuarine habitats has resulted in decreased fishing yield, causing economic hardship for many fishing communities (Walker and Rex-Lopatto 1987; Kahn 1995). At the same time, fishing is impairing the ability of estuarine fish populations to recover suitably from environmental changes. Indeed, fishing practice is widely recognized as one of the major factors causing habitat destruction and modification of community structure in estuaries (Cattrijsse et al. 2002). The synergistic impact of fishing and habitat loss on the quality of estuarine habitats constitutes one of the most important challenges for conservation biologists seeking the restoration of these habitats and sustainable exploitation of estuarine fish.

Despite much progress in developing methods to preserve estuarine habitats, efficient strategies to restore them have yet to be defined based on the life-history characteristics of their inhabitants. Most conservation efforts have focused on two main strategies. The first strategy is the restoration and/or preservation of habitats that supported high species diversity and richness in the past. This approach aims to restore or retain the biological diversity of habitats and the ecological processes that would be

otherwise lost with continuing degradation (Meffe and Caroll 1997). For example, one of the goals of the Chesapeake Bay program is to restore 114,000 acres of submerged aquatic vegetation (SAV) by 2005 (Meffe et al. 1997). Despite clear successes in the restoration program, SAV continue to decline in some major habitats (Orth et al. 2003), and only 76,855 acres of SAV were mapped in the Bay and its tributaries in 2001 (Orth et al. 2002). A major limitation of this approach is that it is rarely possible to restore and preserve all habitats. This is due to prohibitive economic costs and the difficulty in balancing the private cost and the social benefit of preserving habitats (Kahn 1995). For example, habitat preservation may lead to diminishing fishing rates and increasing price of fish on the market. In such condition, fish consumers may lose a source of value (Walker and Rex-Lopatto 1987), whereas commercial fishermen may lose a source of revenue. The difficulty is in determining the optimal level of habitats to preserve for the benefit of future generations, without putting the fishermen out of business. In addition, few restoration programs have a meaningful fishery component when implementing such an approach, even in estuaries where commercial and recreational fisheries have declined or collapsed. As an example, Cattrijsse et al. (2002) reviewed many conservation projects in estuarine habitats, but could not find a single restoration program within Europe that was intended to preserve commercial fisheries or a local fishery stock.

The second strategy determines the optimal habitat requirement for populations based on their historical and current abundances, and preserves those habitats that most satisfy this requirement (Clark et al. 2003; Fourqurean et al. 2003). For example, recent advances in the integration of ecological modeling with geographic information system (GIS) have allowed scientists to improve the prediction of fish abundance based on

habitat affinities (Clark et al. 2003). This approach has promise for managing ecosystems (Clark et al. 2003). However, a major drawback is that abundance may not be a good predictor of habitat-specific fitness for fish, particularly during life stages where mortality is typically high (e.g., larvae and juveniles). There is growing evidence in the field of population ecology that many species have source and sink populations (Pulliam 1988; Pulliam 1996). Therefore, it is difficult to determine whether habitats with high abundance may act as sinks for larval and juvenile fish. It would be more effective to concentrate efforts on restoring source-habitats that may have lower larval and juvenile abundance, but contribute more recruits to the adult stock.

Nevertheless, there is wide agreement that successful biological conservation and management would require ecologists to understand simultaneously the processes of habitat degradation and the response of individual populations to the modification of spatial processes that stabilize vital rates (Hanski and Simberloff 1997; Collinge 2001). Thus, effective conservation would require fisheries ecologists to determine the most essential habitats to restore to assure the persistence of fish populations. Meeting this challenge will also require the development of innovative approaches and tools for the conservation of these natural resources.

1.2. Otolith microchemistry

In the last two decades otolith microchemistry has emerged as an important method to study the environmental history and spatial dynamics of fish populations (Campana 1999). Otolith microchemistry has been applied to identify population structure (Edmonds et al. 1992; Proctor et al. 1995; Begg 1998; Gillanders and Kingsford

2000; Thorrold et al. 2001; Gillanders 2001), to understand patterns of migration (Secor et al. 1995; Kimura et al. 2001; Secor et al. 2001), and to reconstruct environmental conditions experienced by fish populations (Radke and Morales-Nin 1989; Thorrold et al. 1997a). Otolith microchemistry is now viewed as an alternative to traditional tagging in instances where the tagging method is ineffective and the underlying assumptions of its use cannot be met. For example, the application of otolith microchemistry to determine habitat use by larval and juvenile fishes has allowed fisheries ecologists to quantify dispersal rates (Kimura et al. 2001), and relative site fidelity (Thorrold et al. 2001). These quantifications were not possible using traditional tagging methods because of the small size of individual fish and high mortality rates during these early life stages.

Otoliths are fish ear stones that are primarily composed of calcium carbonate in the form of polymorphic aragonite. Otoliths are acellular and their chemistry is not under strong physiological influence as are other fish hard parts (Campana 1999; Secor 1999). Otoliths grow by precipitation of calcium carbonate in a protein matrix. During crystallization, depending on the environment and/or physiology, elements such as Mg, Mn, Sr, and Ba may substitute for Ca, or may be entrapped in the crystal lattice (e.g., the rare earth elements) in trace levels (Amiel et al. 1973; Fritz et al.1990; Geffen et al. 1998; Campana 1999). Similarly, elements such as O may be accumulated into the otolith aragonite with isotopic ratios relating to the temperature of ambient water (Kalish 1991a; Thorrold et al. 1997b). The underlying premise is that the resulting elemental and isotopic composition of otoliths can serve as a distinct natural tag for groups of fish that have experienced different environments. In this context, the validity of this premise relies on the assumption that the physical and chemical environments, within which

groups of fish are living, directly influence the incorporation of trace elements and stable isotopes into the otoliths (Campana 1999; Secor 1999).

Although the elemental composition of otoliths has been shown to reflect water chemistry in laboratory-controlled experiments (Secor et al. 1995; Bath et al. 2000; Milton and Chenery 2001; Martin et al. *in press*), there is little evidence from field-based experiments that otolith microchemistry accurately records water chemistry in marine and estuarine environments. Only one study (Patterson 2003) has directly examined this relationship in a marine environment, the Great Barrier Reef in Australia. However, Patterson's (2003) study was a snapshot in time and the results were equivocal. To my knowledge, no study has directly examined the behavior of trace elements in water and their relationship with otolith trace-element chemistry in estuarine environment.

Trace elements interact with each other during their incorporation in abiogenic and biogenic mineral phases. So, their concentration in the otoliths may vary in different environments. Results from laboratory-experiments cannot simply be extrapolated to fish living in the wild, as they may not model real-world conditions. For example Stoll et al. (2001) observed that [Sr/Ca] dependence on temperature and growth rates in coccolith carbonate varied between culture and field experiments. Indeed, culture experiments based on several coccolith species indicated that [Sr/Ca] ratios depended both on calcification rate and temperature, whereas in field studies [Sr/Ca] showed much larger response to productivity than to temperature. In addition, the spatial scale at which otolith microchemistry is useful may depend not only on the mobility of individual fish, but also on the factors controlling the spatial and temporal variability of trace elements in natural waters. For example, Proctor et al. (1995) found that otolith microchemistry was

not informative in the study of migration of southern bluefin tuna, *Thunnus maccoyii*, potentially due to high homogeneity of the pelagic environment in the Southern Ocean, and low sensitivity of otolith microchemistry to subtle changes in environmental factors.

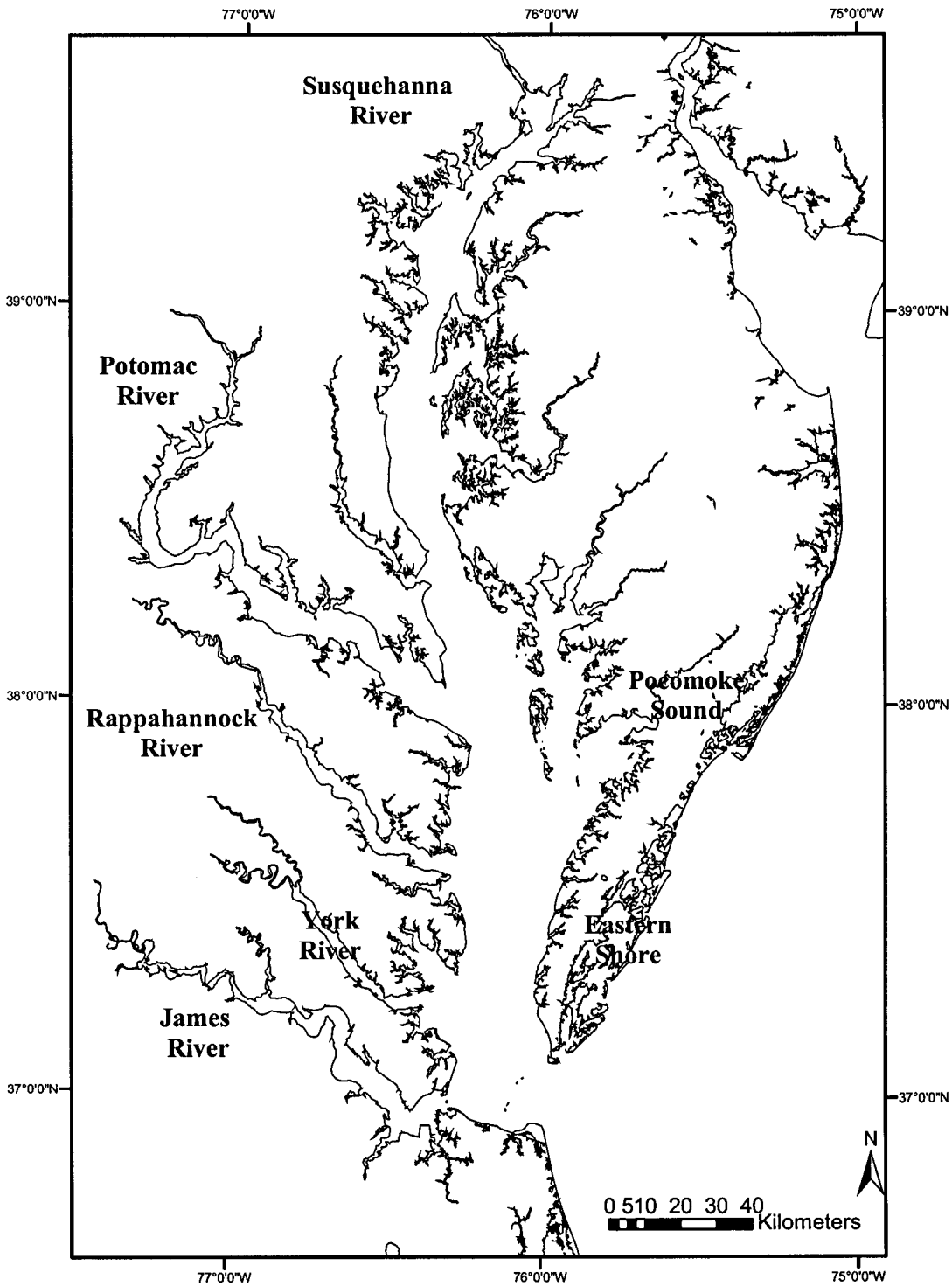
Further, by confining individual fish in a controlled environment, laboratory experiments cannot reproduce the temporal and spatial scales at which ecological factors (i.e., flow regimes, tides, biogeochemical cycling, etc.) interact with fish behavior and physiology to control otolith microchemistry. Thus, future application of otolith microchemistry as a proxy for ambient waters would require: 1) developing field-based experiments to test the assumptions that otoliths do accurately record ambient water chemistry; 2) determining the spatial scale of the variability in otolith microchemistry that would be suitable to study the life history of fish populations.

1.3. The Chesapeake Bay

Chesapeake Bay is located on the mid-Atlantic U. S. East Coast, and is the second largest estuary in the world (Fig.1.1). The physical and chemical properties of the Bay are strongly influenced by the geological diversity of its water sources. The watershed of the Bay encompasses an area of 1.836×10^5 km^2 and is made of four major bedrock types: carbonate rock, crystalline rock, siliciclastic sedimentary rock, and unconsolidated sediments (Langland et al. 1995; Skabral 1995). Weathering of these rocks and freshwater drainage from the basin play an important role in determining the fractionation of trace and minor elements during mixing with oceanic waters (e.g., Sholkovitz and Elderfield 1988; Skabral 1995).

Chesapeake Bay has well defined patterns of salinity along its axes. Most

Fig. 1.1. Map of the Chesapeake Bay showing the locations of the five major tributaries: Susquehanna River, Potomac River, Rappahannock River, York River, and James River.



freshwater input enters the Bay from the western shore, in particular from five major tributaries: the Susquehanna, Potomac, Rappahannock, York, and James Rivers (Fig.1.1). These rivers supply annually an average of 2280 to 2570 m^3/s of freshwater (Goodrich 1988, Austin 2003), but the Susquehanna, Potomac, and James Rivers account for 80% of the input (Valle-Levinson et al. 2001). Freshwater fluxes usually peak in the Bay in March-April and reach their lowest levels in August-September (Valle-Levinson and Lwiza 1997). Coriolis acceleration causes outflow of freshwater toward the West, and inflow of oceanic water toward the East. Thus, salinity increases laterally from the western shore to the eastern shore (Pritchard 1952, Austin 2003). Seasonal variability in river discharges determines the magnitude of the salinity gradient in the Bay longitudinally and laterally, but in general, waters of the Bay show nearly oceanic salinity at its mouth (~29 ppt) and freshwater at its head, the entrance of the Susquehanna River (Austin 2003). This spatial variation in salinity influences the distribution and concentration of trace elements in the Bay, because increase in salinity may cause flocculation of river colloids and fractionation of trace elements along with dilution and mixing (e.g., Powell et al. 1996, Sholkovithz 1978, Sholkovitz and Elderfield 1988, Wen et al. 1999).

The Chesapeake Bay has a very complex bathymetry consisting of both natural and navigational channels, where bottom waters undergo seasonal anoxia. The northern region of the Bay, north of the Potomac River, is deeper than the southern region, which averages 10 m depth (Valle-Levinson and Lwiza 1995; Sholkovitz and Elderfield 1988). High spring freshwater input and warming of surface waters cause stratification in the Bay and an increased consumption of oxygen in bottom waters. The depletion of oxygen

in bottom waters peaks in summer and typically results in anoxia (Taft et al. 1980; Officer et al. 1984; Seliger et al. 1985). These seasonal changes in oxygen of the bottom waters of the Bay play a prominent role in determining the temporal and spatial distributions of redox sensitive trace elements such as Mn and Fe (Eaton 1979; Gavis and Grant 1986).

1.4. Spotted seatrout

Spotted seatrout, *Cynoscion nebulosus*, are estuarine-dependent sciaenids that primarily occur from the Chesapeake Bay to Northern Mexico (Ramsey and Wakeman 1987; Brown-Peterson et al. 1988). Within their geographic range they are spatially subdivided into local populations, and the Atlantic populations have diverged genetically from the Gulf populations (Gold et al. 1999). This regional pattern may reflect historical vicariance resulting from climatic changes during glacial times (Avise 1992), but may also be the result of oceanic currents that prevent movement between the Gulf of Mexico and the Atlantic Ocean (Gold et al. 1999). Most spotted seatrout populations are restricted to their natal estuaries (Music 1981; Baker et al. 1986; Baker and Matlock 1993). They move periodically to coastal waters, but in general these are local spawning or feeding movements in response to change in temperature and salinity. Limited dispersal among estuaries and high natal philopatry may have contributed to low gene flow among estuaries, resulting in spatially and genetically discrete populations (King and Zimmerman 1993; Gold et al. 1999; Wiley and Chapman 2003). In this respect, the Chesapeake Bay population is unique, because despite being genetically isolated from the other populations of the U.S. Atlantic coast (Wiley and Chapman 2003), it is the only

known population that undergoes large-scale spring immigration into its natal estuary and fall emigration outside of its estuary.

Spotted seatrout are batch spawners that have a protracted spawning season. In most areas, they spawn from April to September (Brown-Peterson 2003; DeVries et al. 2003), but in the Chesapeake Bay the spawning period is shorter, extending from May to July (Brown 1981). Spotted seatrout spawn in surface waters with salinities varying from 20 to 37 ppt and temperatures between 24 and 27 °C (Brown-Peterson et al. 1988). After fertilization, floating eggs hatch within 24 to 36 hours, and thereafter the larvae are transported to their nursery habitats where they settle when reaching five to six mm of total length (TL) (Wenner and Archambault 1995, Poling and Fuiman 1999).

Juvenile spotted seatrout are strongly associated with seagrass habitats throughout most of their range (Chester and Thayer 1990; Rooker et al. 1998), however where seagrasses do not occur, in areas of high tidal range (~ 1.82 m) such as in South Carolina and in Georgia estuaries, juveniles nurse in shallow marsh habitats (Weinstein 1979; Wenner and Archambault 1995). Juveniles use these habitats as shelter to minimize risk of being preyed upon by visual predators (Heck and Crowder 1991). Larvae and juveniles have evolved specialized sensory-mechanoreceptor organs to avoid predation while feeding in these habitats (Poling and Fuiman 1999). The spring and summer residence of larval and juvenile spotted seatrout coincides with the peaks in crustacean and fish abundance in these habitats (Livingston 1984). Specifically, juveniles feed mostly on small epibenthic shrimps, copepods, and small fish (Llansó et al. 1998; Murphy et al. 1999). Juveniles stay in these nursery grounds for three to four months before moving to their over-wintering grounds (Wenner and Archambault 1995).

Most spotted seatrout become sexually mature between 270 and 350 mm (TL), with males reaching their maturity at a smaller size than females (Brown-Peterson 2003; DeVries et al. 2003). The maximum age of spotted seatrout varies among estuaries and may be up to nine years (Murphy et al. 1999). In most estuaries adult spotted seatrout primarily reside in shallow seagrass beds, but also can be found around oyster bars, marsh edges, and creek mouths (Wenner and Archambault 1995; Murphy et al. 1999). Tagging studies have consistently shown that adult fish stay close to their natal habitats, with a roaming range of less than 50 km (Iverson and Tabb 1962; Lorio and Peret 1978; Baker et al. 1986; Wenner and Archambault 1995; Music 1981). Also, adult spotted seatrout may show strong spatial structure even within estuaries (Baker et al. 1986; Baker and Matlock 1993).

The abundance of spotted seatrout has declined throughout its range of occurrence (Bortone 2003). This population decline has been hypothesized to be a result of overfishing and habitat loss (Shipp 1986; Patillo et al. 1997; Bortone 2003). Following population decline, commercial catches were restricted or prohibited in various fisheries of the Gulf of Mexico (Murphy et al. 1999; Bortone 2003). Although these policies have lead to a significant decrease in commercial landings in most fisheries, mortality rates of spotted seatrout continue to be high. For example, along the U. S. Atlantic East Coast annual mortality rates of spotted seatrout are among the highest for the species, varying from 70% in South Carolina and Florida to 90% in Georgia (Murphy and Taylor 1994; Wenner and Archambault 1995; Murphy et al. 1999).

In Virginia, commercial landings of spotted seatrout were highest in 1944 reaching 345 metric tons (mt), but fluctuated between 1 and 89 mt from the 1950's

throughout the 1980's (Murphy et al. 1999). High inter-annual variability in the catch is typical of most spotted seatrout fisheries, and appears to correlate with climatic conditions in winter and spring (Merriner 1980). However, the long-term decline of the catches in Virginia coincided with the dramatic declines of seagrass habitats in the Chesapeake Bay (Orth and Moore 1993).

1.5. Objectives

This dissertation research provides a field-based experiment to test hypotheses on otolith microchemistry, and to evaluate the usefulness of otolith microchemistry in addressing current issues in conservation of estuarine-dependent fish and their habitats. The dissertation aims to answer three basic questions:

1) Can the trace-element chemistry of surface waters be used to distinguish habitat use for estuarine and estuarine-dependent fish?
2) Can water chemistry of surface waters predict otolith microchemistry in estuarine environment and, if so, at what spatial and temporal scales?
3) Can otolith microchemistry be used to identify essential seagrass habitats for estuarine and estuarine-dependent fish?

To answers these three questions a study was conducted in Chesapeake Bay because this estuary has: well defined patterns of salinity and dissolved trace and minor elements, and a fish species the spotted seatrout, *Cynoscion nebulosus*, whose life history is closely associated to its natal habitats. The elements Mg, Ca, Mn, Sr, Ba, and La, and the stables isotopes $\delta^{13}C$ and $\delta^{18}O$ were chosen for analysis. Mg, Ca, Mn, Sr, and Ba have been previously used in otolith microchemistry. Although in a laboratory experiment Ennevor

and Beames (1993) demonstrated that La could be absorbed from water and deposited in otoliths, this element has not been previously used to study population structure and environmental history of fish. The quantification of these five elements in surface waters and otoliths was done using a double-focusing sector-field inductively-coupled plasma mass spectrometer (Finningan MAT Element 2 ICP-MS). Stable isotopic ratios were measured using an automated Isoprim Micromass carbonate analyzer. These are two of the most sensitive instruments in the field of analytical chemistry, for elements and stable isotopes. Throughout this research I used robust and conservative statistical methods for the testing of hypotheses and the quantification of the relationship between water chemistry and otolith microchemistry. Thus, results from this research put more emphasis on statistical inferences from observed data rather than their underlying chemical behaviors.

I organized the dissertation based on the three questions, which constitute the objectives of Chapter II, III, and IV, respectively. In Chapter V, I summarize the major findings of the research and discuss their significance for the conservation of seagrass habitat and spotted seatrout in Chesapeake Bay.

CHAPTER II

CAN THE TRACE-ELEMENT CHEMISTRY OF SURFACE WATERS BE USED TO DISTINGUISH HABITAT USE FOR ESTUARINE AND ESTUARINE-DEPENDENT FISH?

2.1. Introduction

Recent advances in trace-element analysis have allowed scientists to distinguish the natal origins of fish based on the chemistry of their otoliths (e.g., Gillanders and Kingsford 2000; Secor et al. 2001; Thorrold et al. 2001). A fundamental assumption of this technique is that there is sufficient spatial variation in the chemistry of the ambient waters and that these waters impart habitat signatures to the body parts of the fish. This assumption has been tested only three times in the laboratory, where otolith Ba reflected water concentrations and Sr was directly influenced by temperature (Bath et al. 2000, Milton and Chenery 2001; Martin et al. in press). Only one study has tested this assumption in the field, albeit over a limited time (Patterson 2003) and the results of this study were equivocal. Patterson (2003) showed that trace-element chemistry differed between oceanic and plume waters of the Great Barrier Reef islands, and that these variations were recorded by the otoliths of *Pomacentrus coelestis*. To my knowledge, this assumption has not been tested in estuaries, nor on a small spatial scale.

Major, minor, and trace-element concentrations and distribution in estuaries are a result of physical and chemical processes that interact to regulate the transmission of dissolved and particulate elements from river to ocean (Wolfe and Rice 1972; Bewers and Yeats 1990; Buffle 1990; Guieu et al. 1998). These processes lead to variability in

elemental concentrations longitudinally along the salinity gradient. Physical mixing of fluvial and marine particulates usually results in the depletion of trace metals in suspended matter with increasing salinity (e.g., Hatje et al. 2003; Zwolsman and van Eck 1999). In the estuarine mixing zone, increased salinity causes flocculation of river colloids and fractionation of trace elements (e.g., Sholkovitz 1978; Powell et al. 1996; Wen et al. 1998). Removal of these elements from the dissolved load is also influenced by biological activity (Zwolsman and van Eck 1999; Nozaki et al. 2001). During spring bloom the concentration of trace metals and lithogenic elements in suspended matter may decrease, whereas the concentration of biogenic elements may increase (Zwolsman and van Eck 1999). For example, in the Scheldt estuary, Zwolsman and van Eck (1999) observed that the spring bloom caused increased Ba in suspended matter, otherwise Ba decreased with increasing salinity. Remobilization of trace metals from particulate matter and sediments is also an important mechanism affecting the chemistry of surface waters in estuaries. Seasonal anoxia, for example, causes reduction and release of trace elements from surface sediment. Process of remobilization may interact with mixing, leading to complex dynamics in the distribution of trace elements along the salinity gradient (e.g Eaton 1979; Paucot and Wollast 1997, Yang and Sanudo-Wilhelmy 1998).

There has been less focus on understanding spatial and temporal variability of minor and trace elements across estuaries. In small and narrow estuaries, rapid cross-sectional mixing may lead to negligible lateral differences in both salinity and the concentration of minor and trace elements (Smith 1977). However, in large estuaries significant lateral variability in the salinity gradient may occur due to the influence of physical processes on outflow of freshwater and inflow of oceanic water. Many studies

depict lateral heterogeneity in water density distribution either due to Coriolis acceleration (Pritchard 1952; Austin 2003) or to the interaction among barotrophic forcing, baroclinic forcing, and bathymetry (Nunes and Simpson 1985; Huzzey 1988; Huzzey and Brubaker 1988; Brown et al. 1991; Valle-Levinson and Lwiza 1995). For example, in a wide estuary such as the Chesapeake Bay the earth's rotation may lead to the modification of the typical two layer-estuarine circulation by forcing mean outflow of freshwater to be confined to the West and mean inflow of oceanic water to the East (Pritchard 1952; Austin 2003). On the other hand, bathymetry may interact with pressure and density gradients leading to near-surface convergence flow over channels of the Chesapeake Bay (Huzzey and Brubaker 1988; Valle-Levinson and Lwiza 1995). In such systems, it is likely that the density and momentum differences between waters may prevent the transfer of trace elements across such interfaces (Shumilin et al. 1993), producing lateral heterogeneity in water chemistry. To my knowledge, no studies have tested whether such physical structure may lead to significant lateral spatial differences in minor and trace elements in estuaries such as Chesapeake Bay. Past studies of estuarine chemistry of minor and trace elements were based on small samples size (Zwolsman and van Eck 1999). Small sample sizes may result in low statistical power preventing the resolution of spatial and temporal differences across estuaries. Moreover, in broad estuaries such as Chesapeake Bay most studies have focused on the chemistry of the deeper waters (channels) with little investigation of shallow waters (e.g., Eaton 1979; Gavis and Grant 1986; Skrabal 1995; Coffey et al. 1997).

Although aquatic ecologists have studied lateral variability of minor and trace elements in sediments, they have overlooked the significance of surface-water variation.

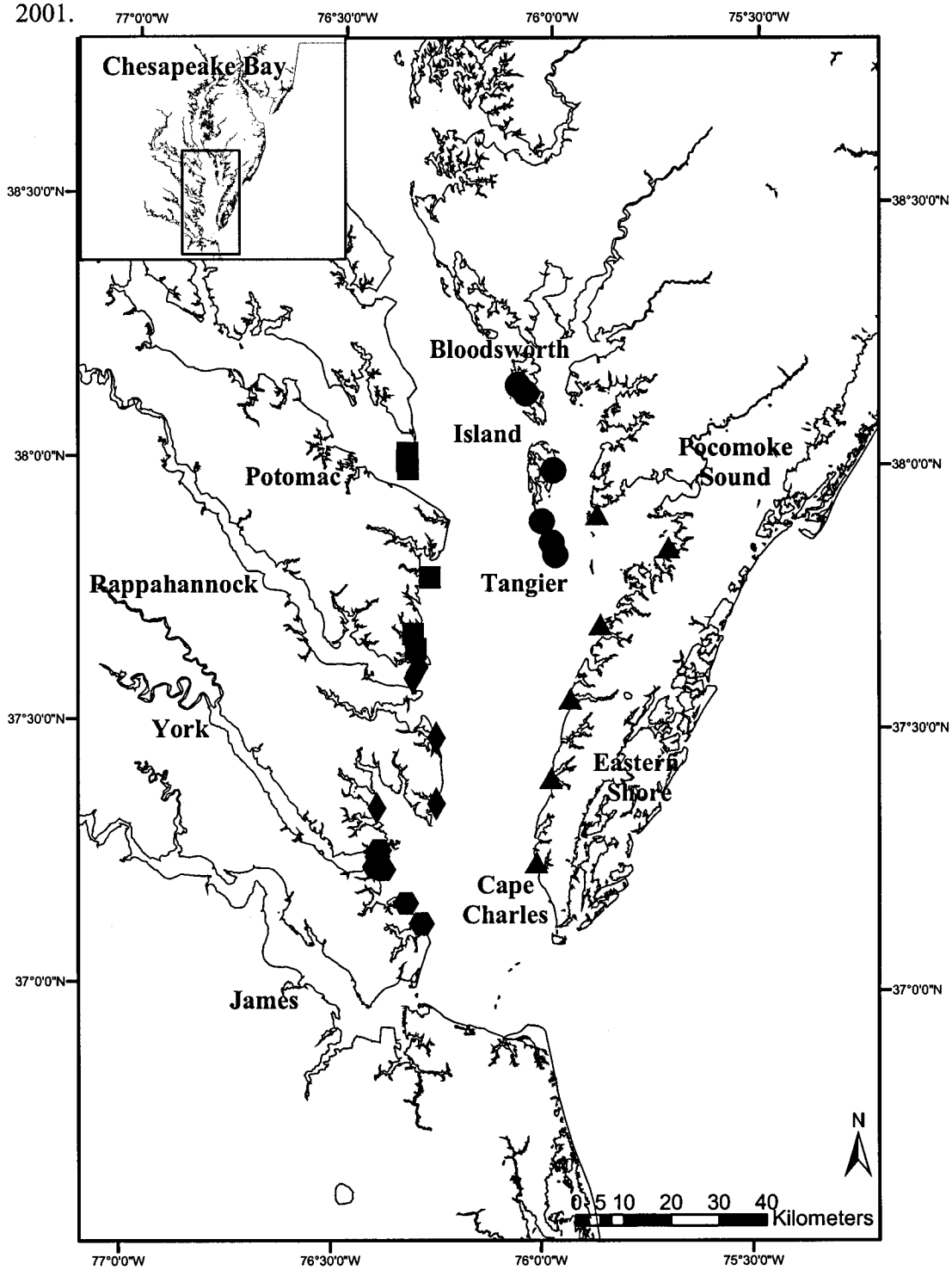
Most scientists have used these minor and trace elements as direct indicators of habitat quality only. In this context researchers identified sources and sink of contaminants (e.g., Coakley and Poulton 1993; Helz et al. 1985; Sinex and Heltz 1981; French 1993) or assessed the impact of pollutants on habitats and organisms (e.g., Koehler 1990; Stronkhorst 1992; Zdanowicz and Gadbois 1990). Scientists have minimized the use of surface water trace-elements as geo-chemical markers that could be used to understand the dynamics and life history of vagile estuarine and estuarine-dependent organisms.

In this study, I hypothesize that physical and biogeochemical processes acting in seagrass habitats of the Chesapeake Bay are spatially independent and that seagrass habitats have their own unique chemical identity. Under my hypothesis, I will show that the chemical variation of dissolved elements in surface waters of these habitats are fully resolvable in space over the sampling period, and allowed the identification of most seagrass beds based solely on water chemistry.

2.2. Studied area

Chesapeake Bay is the largest estuary in the U.S. (Fig. 2.1). Five major tributaries supply most of the fresh water input: the Susquehanna, Potomac, Rappahannock, York, and James Rivers. The mean annual flow of freshwater in the estuary approximates 2570 m^3/s (Goodrich 1988) of which the Susquehanna, the Potomac, and the James Rivers contribute 80 % (Valle-Levinson et al. 2001). The watershed of the Chesapeake Bay is constituted of four major bedrock types: carbonate rock (limestone, dolomite, marble); crystalline rocks (schist, granite, quartzite, gneiss); siliciclastic sedimentary rock (sandstone, siltstone, shale, conglomerates); and

Fig. 2.1. Map of the lower Chesapeake Bay showing the locations of sampling habitats and stations. Five seagrass habitats were sampled for water: Potomac, Rappahannock, York, Island, and Eastern Shore. At each station water samples were collected twice monthly during spring tide from July to September 2001.



unconsolidated sediments (sand and gravel) (Langland et al. 1995). The physical and chemical properties of the Bay are strongly influenced by the geological diversity of water sources (Skrabal 1995).

The Bay has a very complex bathymetry of natural and navigational channels, and shoals. Based on its bathymetry it may be divided in two regions: the deeper upper Bay, north of the Potomac River, basically an estuary of the Susquehanna River which supplies up to 87% of its freshwater (Sholkovitz and Elderfield 1988), and the shallower lower bay, from the Potomac River to the mouth of the estuary, that averages 10 m depth (Valle-Levinson and Lwiza 1995).

2.3. Methods

2.3.1. Sampling site and design

My study covers shallow waters of the lower Chesapeake Bay between 37°00' and 38°20' latitude, an area historically dominated by seagrass beds (Moore et al. 2000). These seagrasses constitute important nurseries for larval and juvenile fish, mollusks, and crustaceans. Based on the physical characteristics and the distribution of these seagrass beds I divided this region in five major habitats (Fig. 2.1):

1) Potomac habitat: mouth of the Potomac River to the northern shore of the Rappahannock River.
2) Rappahannock habitat: mouth of the Rappahannock River to the northern shore of the York River.
3) York habitat: mouth of York River to the northern shore of James River.
4) Island habitat: Tangier island to Bloodsworth island.

5) Eastern Shore habitat: Pocomoke Sound to Cape Charles.

In each habitat, six fixed stations were established along the salinity gradient (Fig. 2.1). I accessed stations using a 21-foot fiberglass boat, and at each station samples were collected twice monthly, during spring tide from July through September 2001. During spring tide, mixing was maximal in the water column (Valle-Levinson et al. 2000) and I could assume that mixing in surface waters was maximum across the estuary. Therefore any spatial differences in chemistry among seagrass habitats reflected minimal differences compared to neap tide conditions.

2.3.2. Water Collection

Water was collected in a quasi-synoptic fashion over four days. In general, it took one day each to sample the Island and Eastern Shore habitats, and two days to sample the three Western Shore habitats. In a given habitat all samples were collected in the same day and over different tidal phases. Thus seasonal samples from a given habitat reflected the variability in dissolved elements due to the effects of locations.

At each station, water was collected at a randomly selected site using clean-method procedures (Sholkovitz and Elderfield 1988; Powell et al. 1996 with some modifications). Each sample was pumped at 50 cm depth using a peristaltic pump (Masterflex 7520-60) and acid washed Teflon tubing. The tubing was maintained at depth using a glass probe weight. While being pumped, water was filtered through a certified Gelman capsule (GWV, 0.45 μm Versapor) to exclude the particulate fraction, but retain the colloidal and dissolved fractions. So, in this study I measured the sum of the colloidal and dissolved fractions and operationally defined these measurements as

total dissolved metal concentration. During the first ten minutes of pumping, water was not sampled, allowing 4-5 sample volumes to purge the system. Thereafter, water was collected in acid-washed high-density fluorinated Nalgene bottles (250 ml) and acidified to pH < 2 using 1 ml of ultrapure HNO_3. After sampling, the filtration system was again allowed to flush completely. Each filter was used to collect 4-6 samples within habitat only. Sholkovitz and Elderfield (1988) observed no sampling artifacts in water samples collected similarly along the salinity gradient in Chesapeake Bay. All sample bottles were stored in double Zip-lock® bags, chilled on ice in the field and refrigerated in the laboratory until analysis.

During water sampling, I also measured temperature, salinity, conductivity, pH (using a YSI 63), DO (using a YSI 55), and depth. The phase of the tide was noted. For continuous, long-term temperature and salinity monitoring, I used HOBO sensors (Onset US PAT 5373346) and microcat-seabird thermosalinographs (SBE 37).

2.3.3. Water analysis

Water samples were prepared for analysis in a class-100 clean room, and elements were analyzed using external calibration with internal standardization (In; Taylor 2001). Water samples were diluted fivefold by spiking a sub-sample of 200 µl with 800 µl of internal standard, resulting in an aliquot of 1000 µl solution and 4 ppb In concentration. From each aliquot, Mg, Mn, Sr, and Ba were quantified using a double focusing sector field inductively-coupled plasma mass spectrometer (Finningan MAT Element 2 ICP-MS). Mg, Mn, Sr, and Ba were selected because they are the most commonly used in otolith microchemistry. All water samples collected in a given week were analyzed on

the same day. However, aliquots were randomized within trays to minimize the effect of instrument drift. Sample solution was introduced using a PFA microflow nebulizer (50 μL/min) and a PFA spray chamber. Acquisition parameters are summarized in Table 2.1.

High purity stock standards (Charleston, SC) were used to prepare multielement calibration standard solutions. Calibration standards were made by diluting the stock standard solution with 1% ultrapure HNO_3 (by weight) to match typical concentration of Mg, Mn, Sr, and Ba in estuarine waters. Concentration of In in all standard solutions was 4 ppb. Analytical blank solutions were made up of ultrapure HNO_3 diluted to 1% with milli-Q water. In addition, the procedure was monitored by a procedural blank (1% ultrapure HNO_3 and 4 ppb In solution) and a quality control check standard solution sequentially after the analysis of every six aliquots.

Calibration curves were established based on known concentrations of the analytes in the calibration standard solutions (categorized as low medium, and high concentration in Table 2.1). After acquiring ion intensity data from the mass spectrum, the ion intensity measurement was properly corrected for background interferences based on the analytical blank, and for matrix effects and instrument drift based on the control check standard solution. Thereafter, the ratio of the analyte ion intensity to In ion intensity was plotted against the known concentration of the analyte in the calibration standards (Taylor 2001). Least-square regression was fitted to the data with goodness of fit (R^2) greater than 0.999. The data was further corrected for procedural blank by forcing the regression line to pass by 0. Finally, concentration of each analyte was calculated from the linear equation derived for each calibration curve. Method detection

Table 2.1. Summary of acquisition parameters, concentration of standards (low=L, medium= M, high= H), method detection limit (MDL), and mean estimates of precision (% RSD, relative standard deviation) from ICP-MS analysis of water samples collected in seagrass habitats of Chesapeake Bay from July to September 2001.

Isotopes	^{115}In	^{137}Ba	^{25}Mg	^{55}Mn	^{88}Sr	^{115}In
Concentration unit	ppb	ppb	ppm	ppt	ppb	ppb
Resolution	Low	Low	Medium	Medium	Medium	Medium
Mass window	5	5	150	5	150	150
Settling time (ms)	0.0010	0.0010	0.3000	0.0010	0.0010	0.3000
Sampling time (ms)	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200
Samples per peak	200	200	15	15	15	15
Method mass offset	0.0009	0.0002	0.0011	0.0007	-0.0001	0.0007
Standard (L)	4.0100	1.0200	20.0700	50.7900	39.9500	
Standard (M)	4.0100	10.0200	106.0100	250.6900	196.6100	
Standard (H)	4.0200	15.0600	212.4900	503.1800	397.6700	
MDL		0.0000	0.0037	5.0267	0.0260	
% RSD		1.1250	3.9000	1.8000	1.8500	

limit (three times the standard deviation of procedural blank signal, MDL) and precision (relative standard deviation from repeated measurement of standards, % RSD) achieved for each element are presented in Table 2.1.

2.3.4. Statistical analyses

To test the hypothesis that there were no significant spatial and temporal differences in the chemistry of surface waters in the lower Chesapeake Bay, I used a 3 x 5 factorial multivariate analysis of variance (MANOVA) based on Mg, Mn, Sr, and Ba. Based on the experimental design, the sampling unit was a day of sampling in a given week within a given habitat. Therefore, I performed the MANOVA using the weekly-mean of each response variable within habitat. A univariate form of the model is presented below:

$$y_{ijk} = \mu + \alpha_i + \beta_j + \alpha\beta_{ij} + \varepsilon_{ijk}$$

where, μ is the overall mean

α_i is the effect of the i^{th} habitat (i = 1 to 5),

β_j is the effect of the j^{th} month (j= 1 to 3)

$\alpha\beta_{ij}$ is the interaction between habitat and month

ε_{ijk} is the sampling error in the i^{th} habitat, the j^{th} month, and the k^{th} week (k= 1 to 2).

Univariate normality for each variable was tested using the Shapiro-Wilk test, whereas homogeneity of variance-covariance matrices was tested using Bartlett's maximum likelihood ratio test in SAS 2002[2]. Multivariate tests of significance were based on

[2] SAS 2002. Statistical software released by SAS Institute Inc. Cary, NC 27512, USA.

Pillai's trace statistic, which is particularly robust to deviations from multivariate normality when the analysis is performed on balanced data (Quinn and Keough 2002). Student-Newman-Keuls (SNK) multiple range test was used to determine which habitats were different and what elements contributed to the observed difference (Khuel 1994).

I used a non-parametric discriminant analysis, the *k*-Nearest Neighbor method (*k*-NN), to predict the accuracy of classification of individual water samples to their collection habitat. This method does not require multivariate normality and homogeneity of variance-covariance matrices (SAS 1988; Kattree and Naik 2000). I determined classification accuracy from the *k*-NN using a cross-validation method (Jacknife, leave one out; Lachenbruch 1975). Using simulations, I determined that $k = 4$ yielded the smallest total error rate after cross-validation, therefore results of the *k*-NN were based on this value.

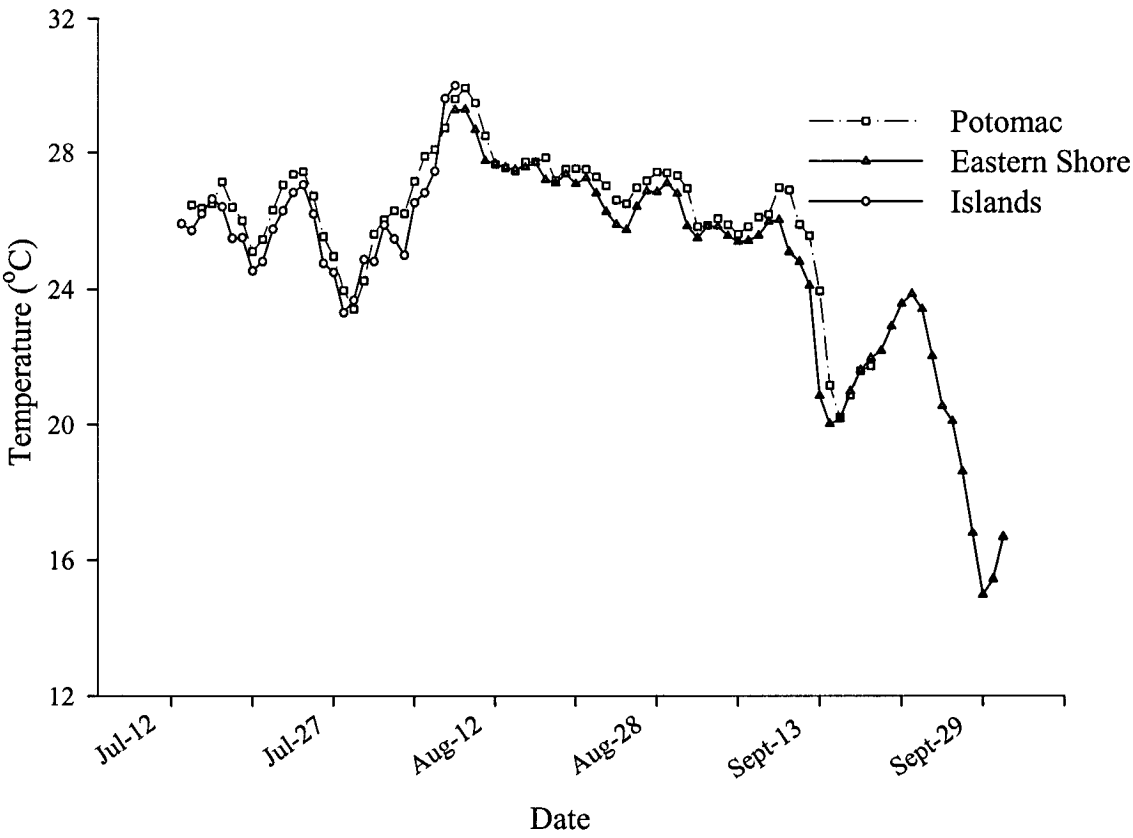
In this study all statistical analyses were performed using the SAS statistical software after averaging daily observations in river mouth and excluding all extreme outliers. Values that were greater or smaller than three times the interquartile range (IQR) of each variable in a given habitat were defined as extreme outliers.

2.4. Results

2.4.1. Variation of temperature, salinity, DO, and pH

Temperature varied coincidentally across all seagrass habitats following a seasonal pattern over the three months of sampling (Fig. 2.2). Temperatures averaged 25.7 °C in July, 27.4 °C in August and 23.1 °C in September. Thus, elements influenced by temperature were affected similarly, and therefore temperature cannot be invoked as

Fig. 2.2. Mean daily temperature measured in three seagrass habitats from July to September 2001.



an explanation of variations in elemental concentrations between seagrass habitats at any given time.

Salinity was significantly different among habitats with moderate seasonal variation (Fig. 2.3a). Mean salinity was lower in the Island and the Potomac habitats; within habitat variability across months were minimal in the Island and the York. Thus, the effect of salinity on trace element concentration in the Island and the York was the most consistent over time.

Concentration of DO and pH measured during the sampling period showed slight temporal and spatial variation (Fig. 2.3b, 2.3c). Mean and standard error of DO in surface waters demonstrated an ample supply of oxygen in the water column for all habitats. In fact, the water column in these shallow waters was well mixed during the sampling period. pH was alkaline and typical of seawater with an overall mean of 8.11.

2.4.2. Mixing patterns and variability of Mg, Mn, Sr, and Ba

Figure 2.4 shows the variation of Mg, Mn, Sr, and Ba along the salinity gradient. As anticipated Mg, Sr, and Ba demonstrated conservative behavior with increasing salinity across months. The elemental composition in samples from the northern habitats, the Island and Potomac, were distinctly different from the southern habitats: the Rappahannock, the York, and the Eastern Shore (Fig. 2.4a). Mg concentration in samples from the northern and southern habitats showed similar spatial patterns to that of Ba along the salinity gradient (Fig. 2.4b). In contrast to Mg and Ba, Mn exhibited non-conservative behavior along the salinity gradient (Fig. 2.4c). The non-conservative behavior of Mn suggests internal cycling of Mn within seagrass habitats as also observed

Fig. 2.3. Spatial and temporal variation in salinity, dissolved oxygen (DO), and pH measured in surface water of seagrass habitats of Chesapeake Bay from July to September 2001.

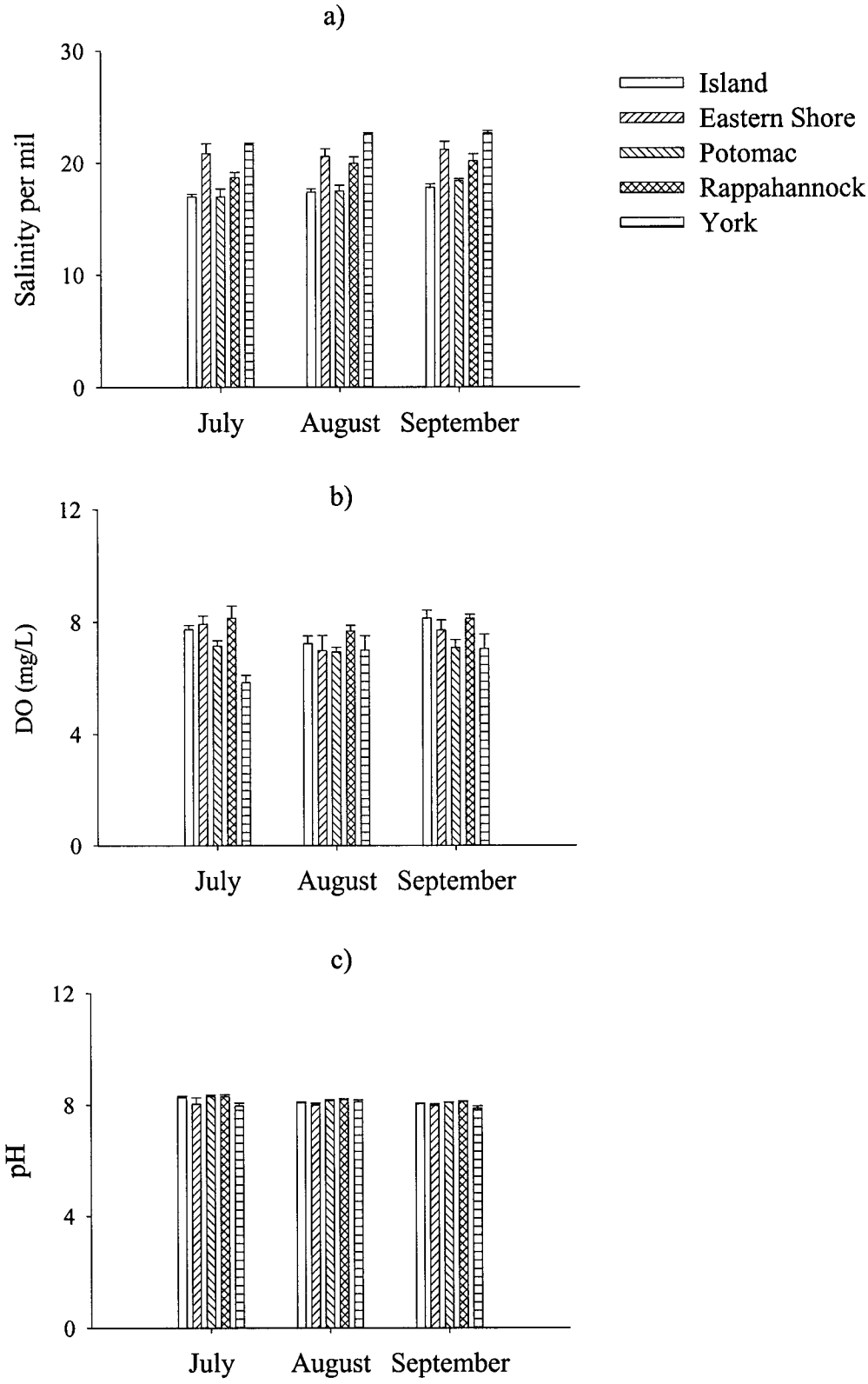


Fig. 2.4a. Variation of Sr, Ba, and salinity measured in surface waters of seagrass habitats in Chesapeake Bay.

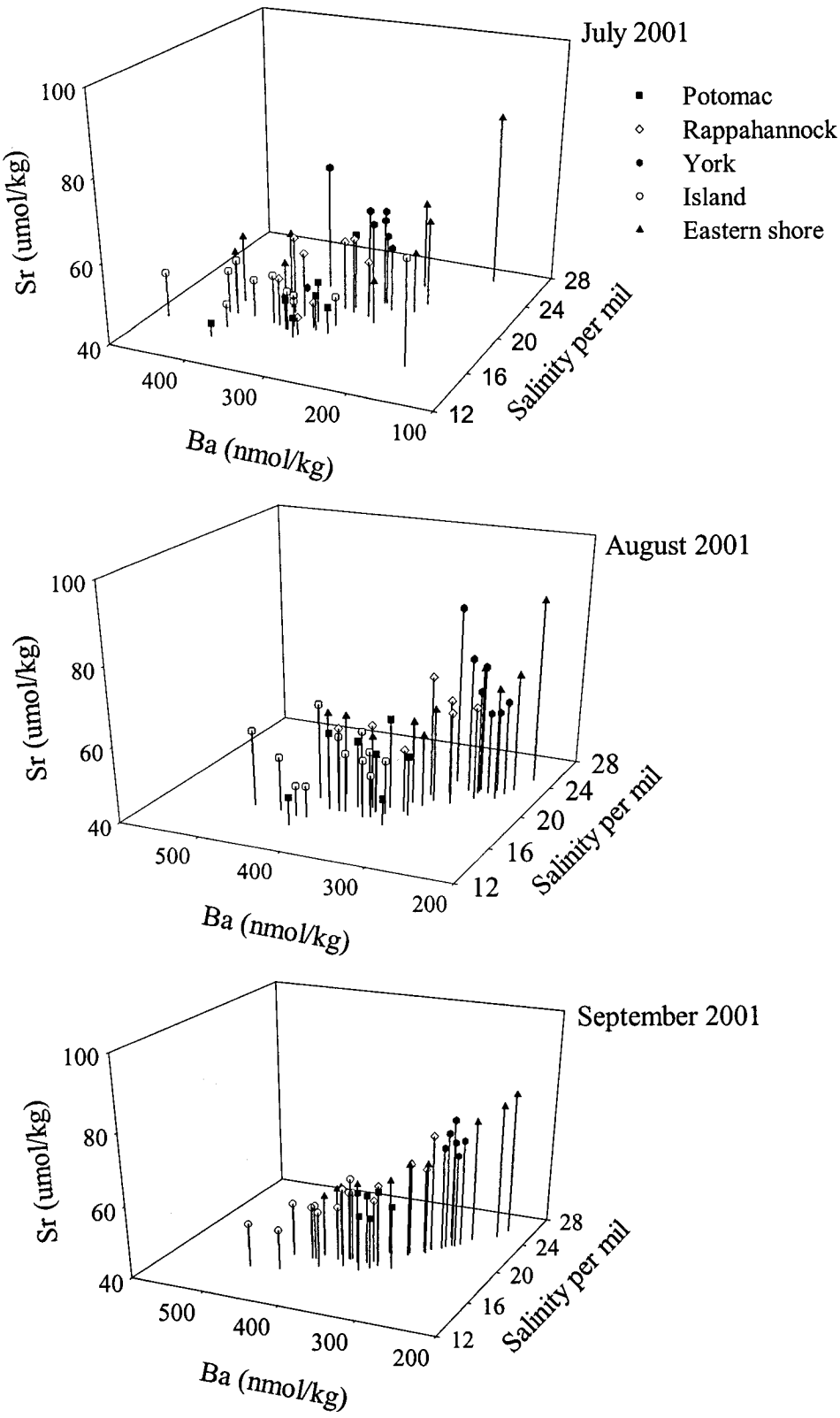


Fig. 2.4b. Variation of Mg, Sr, and salinity measured in surface waters of seagrass habitats in Chesapeake Bay.

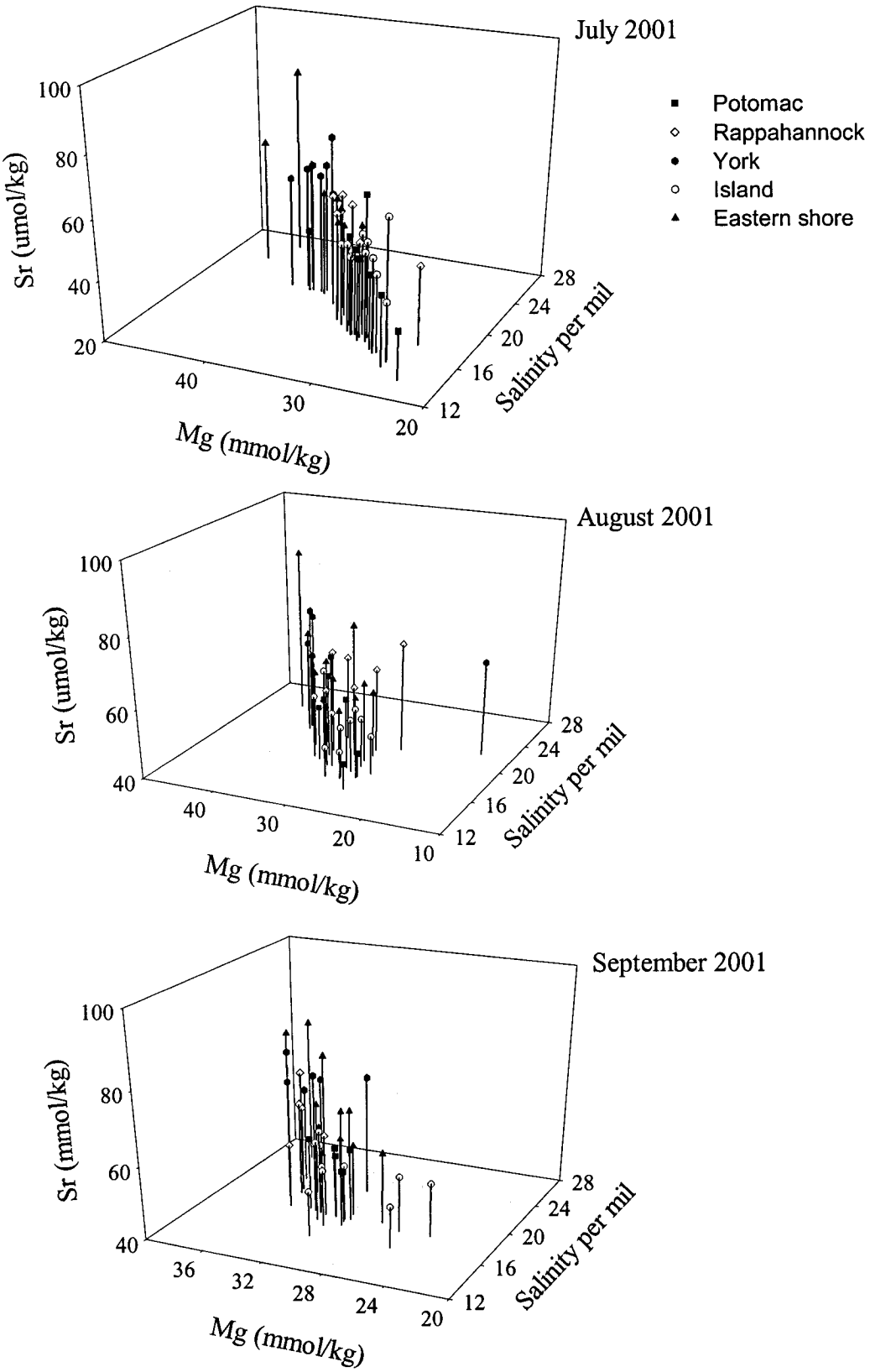
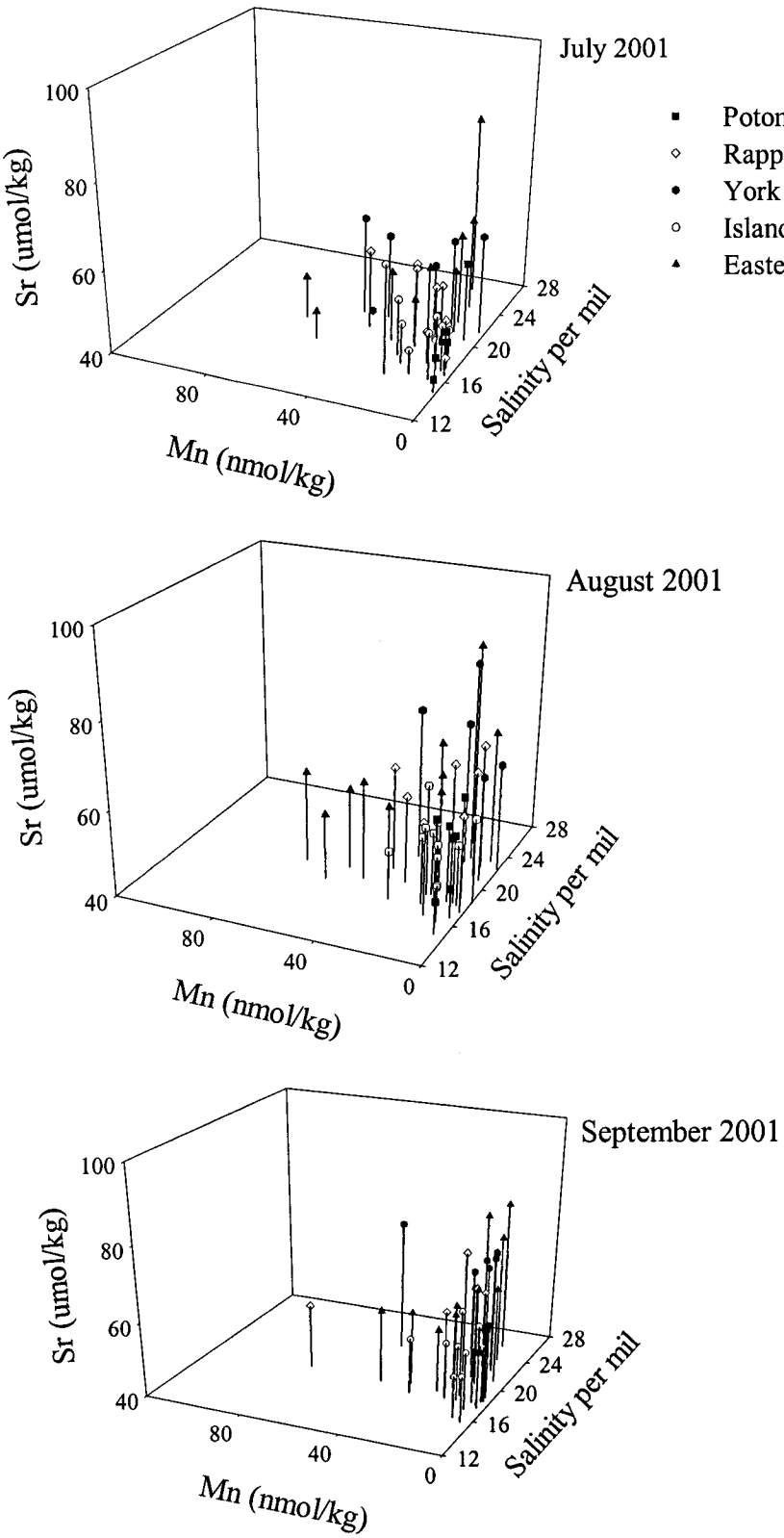


Fig. 2.4c. Variation of Mn, Sr, and salinity measured in surface waters of seagrass habitats in Chesapeake Bay.



by Eaton (1979) and Sholkovitz et al. (1992). Their studies suggested that Mn was released from deep-water anoxic sediments during the summer months and that this flux of Mn to the surface waters dominates the delivery of Mn to the seagrass beds. Although the salinity gradient accounts for much of the spatial difference in elemental composition it does not explain the composition in the Island habitat, which is unlike the other habitats. This difference might be due to the constant salinity throughout the sampling period in the Island habitat, but also as Mn behavior suggests, other factors might interact to lead to this spatial differentiation.

2.4.3. Analysis of variance

Viewed individually the trace elements follow expected trends. Although the picture provided by these elements is interesting, a multi-element, multivariate approach highlights spatial differentiation in chemistry on a finer scale. Table 2.2 presents the results of the two-way MANOVA based on the weekly means of Mg, Mn, Sr, and Ba within habitats. The weekly means of each variable were normally distributed within habitat and within month, therefore I assumed multivariate normality (Quinn and Keough 2002). Further, based on the likelihood ratio test, I found that the variances were homogeneous among habitats ($\chi^2 = 25.879$, $df = 20$, $p = 0.1698$) and among months ($\chi^2 = 49.794$, $df = 40$, $p = 0.1379$). Thus, I conclude that for these four elements MANOVA could be validly used to test my hypothesis.

The MANOVA results showed no significant interaction between month and habitat (Table 2.2). These results suggested that the spatial difference in the chemistry of seagrasses were independent of time. Therefore, though the concentration of these

Table 2.2. Two-way MANOVA results for Mg, Mn, Sr, and Ba measured in surface waters of seagrass habitats of Chesapeake Bay from July to September 2001.

Source	Value	F	Numerator df	Denominator df	P
Habitat	1.95	3.58	16	60	0.0002
Month	0.95	2.96	8	26	0.017
Habitat x Month	1.48	1.1	32	60	0.3621

Note: All tests were based on the Pillai's trace statistic.

elements varied temporally in the Bay, the chemical and physical processes that regulated their spatial distribution remained the same.

Once differences among habitats had been identified, I performed pairwise comparison of habitats based on the SNK multiple range test on each of these variables, Mg, Mn, Sr, and Ba to isolate which habitats were different (Table 2.3). The SNK tests confirmed the uniqueness of the Island as it differed significantly from all habitats in Ba, from all habitats but the Rappahannock in Mn, and from all habitats but the Potomac in Sr. The Potomac was significantly different from all habitats in Mn and had the smallest mean concentration for this trace element. As expected, the York had the lowest mean Ba concentration and was significantly different from all habitats, but was similar to the Eastern Shore in Mn, and to the Eastern Shore and the Rappahannock in Sr.

However, the SNK results for Mg were inconsistent with the MANOVA by exhibiting a significant interaction between month and habitat. The Mg results illustrated the importance of using MANOVA. Because MANOVA combined all four variables, Mg, Mn, Sr, Ba, to derive a composite variable (Grimm and Yarnold 2000), it is possible to identify and quantify differences between seagrass habitats that are unresolvable by univariate analysis. Indeed, the Pillai's trace test provided a more powerful test for interaction, showing that in the multivariate space differences in habitat and month are independent.

2.4.4. Discriminant analysis

Having established differences among habitats independently of month using MANOVA, I further quantify these differences using the *k*-NN discriminant function

Table. 2.3. Two-way ANOVA and SNK multiple range pairwise test results for Mg, Mn, Sr, and Ba measured in surface waters of seagrass habitats of Chesapeake Bay from July to September 2001.

a) Mg

Source	df	MS	F	P
Habitat	4	61.39	47.12	0.0001
Month	2	0.57	0.44	0.6539
Habitat*month	8	5.84	4.48	0.0061

b) Mn

Source	df	MS	F	P
Habitat	4	343.57	12.76	0.0001
Month	2	27.82	1.03	0.3799
Habitat*month	8	12.57	0.47	0.8609
SNK grouping		Mean	*n*	Habitat
	A	23.16	6	York
	A	22.59	6	Eastern Shore
B	A	15.81	6	Rappahannock
B		12.12	6	Island
	C	5.06	6	Potomac

c) Sr

Source	df	MS	F	P
Habitat	4	190.93	12.58	0.0001
Month	2	267.51	17.63	0.0001
Habitat*month	8	2.51	0.17	0.9926
SNK grouping		Mean	*n*	Habitat
	A	66.23	6	York
B	A	62.83	6	Eastern Shore
B		60.12	6	Rappahannock
	C	54.00	6	Island
	C	53.13	6	Potomac

Table 2.3. "Continued"

d) Ba

Source	df	MS	F	P
Habitat	4	11047.70	16.89	0.0001
Month	2	105.17	1.62	0.2314
Habitat*month	8	298.39	0.45	0.8681
SNK grouping		Mean	*n*	Habitat
	A	396.6	6	Island
	B	347.81	6	Potomac
	B	320.57	6	Rappahannock
	B	320.47	6	Eastern Shore
	C	280.18	6	York

Note: Habitats with the same letters (A, B, C) were not significantly different.

analysis. The *k*-NN results in Table 2.4 show that the Islands and the York had the highest accuracy of classification followed by the Potomac and the Eastern Shore. Samples in the Rappahannock were very poorly classified, but this is consistent with the results of the SNK test, which showed that this habitat was not significantly isolated from the other habitats in terms of elemental composition. Classification rates in the Potomac and the Eastern Shore were moderate, but very satisfactory when considering that due to random chance alone, there is only a probability of 0.20 to classify a sample correctly to its collection habitat. These rates were obtained after cross-validation, and thus they are unbiased estimates. High accuracy in allocating samples to the York habitat is a result of mixing between oceanic and fluvial waters. Compared to the other habitats, the York is like the Eastern Shore, which is an oceanic end member, but differs from the latter by the greater influence of fresh water. What was very striking was that I could predict with such high accuracy samples coming from the Island habitat. As discussed above, the clear separation of the Island from the eastern and the western shore habitats may not be due simply to mixing processes only, but rather to the interaction of mixing and other physical and chemical processes.

2.5. Discussion

The chemistry of seagrass habitats along and across the Chesapeake Bay are significantly different and the variation in chemistry cannot be solely attributed to salinity. Other factors such as redox cycling of Mn may also contribute to these differences. Because the chemistry of the dissolved load in the Island is distinct from that of western and eastern shore habitats, spatial variations are fully resolvable across all

Table 2. 4. Results of non-parametric discriminant function analysis using the *k*-nearest neighbor method (*k*-NN, *k*=4) where water samples were classified to the original collection habitats based on the concentration of Mg, Mn, Sr, and Ba.

Sample source	Cross-validation accuracy (%)					
	Island	Eastern shore	Potomac	Rappahannnock	York	Other
Island (*n*=32)	**81.3**	3.1	15.6	0.0	0.0	0.0
Eastern shore (*n*=30)	10.0	**60.0**	3.3	6.7	20.0	0.0
Potomac (*n*=21)	23.8	0.0	**71.4**	4.8	0.0	0.0
Rappahannnock (*n*=19)	5.3	31.6	15.8	**36.8**	10.5	0.0
York (*n*=17)	0.0	11.8	0.0	5.9	**82.4**	0.0

Note: Percentage of classification of water samples were obtained after Jacknife Cross-Validation.
Other = category of water samples that could not be classified to either habitat.

seagrass habitats in the Bay.

The dissolved elemental chemistry among seagrass habitats in the lower Chesapeake Bay is spatially different along and across the estuary. As in any wide estuary, I anticipated variation between southern and northern habitats as well as between the eastern and western shores. It is well known that during estuarine circulation, progressive mixing of freshwater to oceanic water leads to depletion of trace metals in the dissolved load along the salinity gradient (e.g., Guieu et al 1998, Zwolsman and van Eck 1999). Further in a wide system, such as the Chesapeake Bay, Coriolis acceleration may modify typical estuarine circulation causing outflow of freshwater (e.g from the Susquehanna, Potomac, Rappahannock, York, and James Rivers) toward the western shore and inflow of oceanic water toward the eastern shore (Pritchard 1952; Austin 2003). This may result in a lateral density gradient and consequently, as I demonstrated in this study, in a heterogeneous distribution of dissolved elements from the western to the eastern shore. However, the lateral density gradient cannot alone explain the difference between the chemistry of seagrass habitats. For the elements under investigation, beside salinity, competing complexation reactions and redox cycles may interact to produce the level of spatial variability observed both along and across the estuary, including the uniqueness of the Island habitat.

The spatial distribution and concentration of Mg and Ba are consistent with conservative behavior of these elements in estuaries, but they also underlie subtle differences resulting from competing reactions between these elements in seagrass habitats. In the Chesapeake Bay, dissolved Ba concentration typically reaches a maximum (300-400 nmol/kg) between 5 and 10 ppt (Coffey et al. 1997). These peaks

derive from the release of Ba from riverine particle matters by exchanges with Mg^{+2} and Ca^{+2} in oceanic waters (Hanor and Chan 1977, Hilmar and Kogut 1999). In this study I found similar levels of dissolved Ba in the Island and the Potomac habitats. These two habitats are located in the lower Bay. Their Ba concentrations may be simply the result of physical mixing of fluvial and oceanic particulates (Zwolsman and van Eck 1999). However, they may also correspond to desorption of Ba from river sediments deposited in periods of high river discharge to seagrass habitats either by storm events, or high winter river flows. Under such conditions, sediment accumulated in seagrasses would slowly release Ba^{+2} in the summer by exchange with seawater ions, such as Mg^{+2}, when salinity increases and freshwater discharge rates are low. These mechanisms were previously identified by Caroll et al. (1993) in sediment deposited in mangrove habitats and on islands of the Ganges-Brahmaputra mixing zone in the Bay of Bengal. Coffey et al. (1997) noted that such large releases of Ba within estuary are characteristics of the Chesapeake Bay. These authors argued that salt marshes of the Bay behave as storage sites in periods of high supply of particulate Ba. The uniqueness of the chemistry of the Island habitat may be a direct effect of these processes. The Island habitat is located in mid-bay and in the transition zone between the shallow and the deeper topography where the Susquehanna River accounts for 87% of the freshwater input (Pritchard 1952, Sholkovitz and Elderfield 1988). River discharges from the Susquehanna usually peak in the spring, corresponding to snow melt within the watershed. Thus the geographical location of the Island makes it a suitable sink for winter sediments of the Susquehanna River. The dynamics of surface-water chemistry of the Island may reflect the greater influence of river flow and sediment loading of the Susquehanna River.

In contrast to Mg, Sr, and Ba, Mn is a redox-sensitive element whose concentration varies seasonally in the Chesapeake Bay reaching a peak in summer. Mn concentration measured in this study reflected the reduction of Mn^{+4} in surface sediments and bottom waters and subsequent transport of Mn^{+2} into surface waters and shallow seagrass habitats of the Bay (Eaton 1979, Gavis and Grant 1986, Sholkovitz 1992). These processes are prominent in the Bay when suboxic and anoxic conditions develop in spring and summer (Taft et al. 1980, Seliger et al. 1985). Eaton (1979) demonstrated that remobilization of Mn from reducing sediments controlled most of the supply of Mn into surface waters of the Bay. Gavis and Grant (1986) suggested this supply of Mn^{+2} also originated from the reduction and dissolution of oxidized manganese particles formed in deep anoxic water of the Bay. In this study, the magnitude of these processes varies at very fine spatial scale leading to non-conservative behavior of Mn and significant difference in its concentration in seagrass habitats that are separated by 9 to 50 km both along and across the estuary.

The discrimination of seagrass habitats based on their chemistry has important ecological implications. First, differential water masses among habitats suggest that fish exposed to these waters will themselves demonstrate differences in otolith microchemistry that can be used to study the life history of sub-populations of fish inhabiting the seagrass habitats. Otoliths are accretions of calcium carbonate in a protein matrix (aragonite) where elements such as Mg, Mn, Sr, and Ba can be incorporated by exchange with Ca. An inherent property of otoliths is that once an element is deposited, it is recorded permanently. Moreover, otoliths reflect the chemistry of ambient water for elements that are not physiologically regulated such as Mn, Sr, and Ba (Campana 1999).

Recent laboratory experiments have demonstrated clearly there is a linear relation between water chemistry and otolith microchemistry for Sr and Ba (Bath et al. 2000, Milton and Chenery 2001, Martin et al. in press), but this relation was dependent on temperature for Sr. Given the variability seen in this study I expect that otolith microchemistry will reflect water chemistry while also reflecting small-scale spatial differences in Mn, Sr, and Ba. Further, because seagrass habitats experienced similar temperature in the Bay, temperature will not be a confounding factor in spatial differences observed in otolith microchemistry.

2.6. Conclusion

Using both parametric and non-parametric statistical methods I showed significant spatial difference in the chemistry of surface waters longitudinally and laterally in the lower Chesapeake Bay. Despite temporal variability, seagrass habitats were distinct not only because of the influence of salinity but also due to competing chemical reactions and redox control of Mn. The chemistry of the York was distinct, but this was mostly due to the effects of physical mixing on the distribution of trace elements in the Bay. The chemistry of the Island habitat was unique, potentially because of the influence of Coriolis acceleration and river discharges from the Susquehanna River. Finally, my results suggest that fish that live in these seagrass habitats for prolonged periods of time experience different water masses. Therefore, it may be possible to use otolith microchemistry to determine habitat-specific residence for estuarine and estuarine-dependent fish. This has important management implications because it may lead to determination of the most important essential seagrass habitats for these

populations, and likewise a better restoration strategy may be defined to protect and preserve seagrass communities.

CHAPTER III

RELATING WATER CHEMISTRY TO OTOLITH MICROCHEMISTRY IN A COASTAL PLAIN ESTUARY

3.1. Introduction

The use of trace elements in otoliths, as tracers of water mass chemistry, relies on the premise that otolith microchemistry accurately records the water chemistry experienced by fish throughout their lives (Edmond et al. 1992; Thresher et al. 1994; Proctor et al.1995; Thorrold 1997a; Begg et al. 1998; Thorrold et al. 2001). To date, no study has directly tested the validity of this assumption. Due to the lack of field corroboration and the difficulties in designing a field-based test, recent research has focused on laboratory-based experiments for testing the assumption that otoliths do accurately record the chemistry of habitats. These laboratory-controlled experiments have generated a growing body of evidence demonstrating that there is a direct and predictable relationship between water chemistry and otolith microchemistry (Fowler et al. 1995; Secor et al. 1995; Farrel and Campana 1996; Gallahar and Kingsford 1996; Bath et al. 2000; Milton and Chenery 2001; Martin et al. in press). For example, Secor et al. (1995) showed that the ratio of [Sr/Ca] in otoliths of juvenile striped bass was positively correlated with salinity. Likewise, Gallahar and Kingsford (1996) observed that [Sr/Ca] in otoliths of *Girella eleveta* increased with increasing Sr in water. Bath et al. (2000) and Milton and Chenery (2001) found predictable fractionation between water and otolith [Sr/Ca] and [Ba/Ca]. Specifically, Bath et al. (2000) demonstrated that [Sr/Ca] exhibited linear relations that were dependent on temperature, whereas [Ba/Ca] showed a linear

relation independent of temperature.

Though laboratory experiments allow the testing of specific hypotheses in a controlled environment, they also create artificial conditions that may depart from conditions occurring in the field. For example, Bath et al. (2000) set the water [Sr/Ca] significantly higher in test water (15.21-22.80 mmol/mol in average) than that of natural seawater (8-9 mmol/mol). Further, these experiments do not reproduce the scale at which physical and chemical factors interact to control the environmental variability that individual fish experience in the wild. In estuaries, diurnal and fortnightly tidal cycles, river discharges, gravity, Coriolis acceleration, convergence flow, etc. interact to determine spatial and temporal distribution of trace elements (e.g Smith 1977; Brown et al. 1991; Shumilin et al. 1993; Paucot and Wollast 1997). In such dynamic systems the the uptake by fish of chemicals in the water would be determined not only by the concentration of trace elements, but also by the interaction of these physical processes. Moreover, trace elements interact within one and other during their incorporation in biogenic mineral phases, such as in otolith aragonite, and the effect of this interaction may vary with a given environment (e.g., Stoll et al. 2001). All these factors, chemical, biological, and physical have the potential to cause major discrepancies between field and laboratory experiments.

To my knowledge, no experimental studies on otolith trace-element microchemistry have validated their results by using alternative methods simultaneously on the same fish. As an example, many laboratory-experiments showed that otolith $\delta^{18}O$ is accumulated under near equilibrium, and that otolith $\delta^{18}O$ may be used to reconstruct the ambient temperature experienced by fish (Kalish 1991a,1991b; Radtke et al. 1996;

Thorrold et al. 1997b), but to date no studies have used otolith $\delta^{18}O$ to validate the effect of temperature on otolith [Sr/Ca]. Because trace elements interact within one and other, an independent validation procedure would be necessary for the extrapolation and application of results originating from laboratory experiments.

In this study I sought to determine: 1) how the concentration of trace elements in otoliths reflect small-scale temporal and spatial changes in water chemistry within estuaries; 2) Is there a predictive relation between water chemistry and otolith microchemistry and at what spatial scale does it occur? It is critical that these questions be answered in the field in order to use otolith microchemistry as a proxy for changes in water masses and to reconstruct the environmental life histories of fishes. Further, it is of practical value to determine whether there is a predictive relation between water chemistry and otolith microchemistry. A predictive relation is causative, meaning if we know water chemistry in the field, then we can estimate otolith microchemistry without the necessity of establishing an otolith baseline microchemistry by sampling fish directly. When a predictive relation does not exist, then we must establish an otolith library to adequately study life history and population dynamics (Wells et al. 2003). Acquisition of otolith-microchemistry libraries is expensive and time-consuming compared to establishing water chemistry.

In addressing the in situ relation between otolith and water chemistry, I chose a species that is closely associated with its habitat, spotted seatrout (*Cynoscion nebulosus*). Spotted seatrout are estuarine-dependent fish that have developed a strong adaptation with seagrass habitats in most estuaries (McMichael and Peters 1989; Chester and Thayer 1990, Rooker et al. 1998). Tagging studies have consistently shown that adult spotted

seatrout move little within an estuary, rarely between estuaries, and generally stay close to their natal habitats (Iverson and Tabb 1962; Lorio and Peret 1978; Music 1981; Bryant et al.1987; Wenner and Archambault 1995). Music (1981) observed that tagged spotted seatrout move an average 8.9 km in Georgia estuaries. Bryant et al. (1987) reported a maximum movement of 6 km from a tagging site in Florida estuaries. Thus, spotted seatrout can display strong spatial structure within estuaries (e.g., Baker and Matlock 1993). Juvenile spotted seatrout have even less propensity to move because they rely on seagrass habitats as a source of food and as refuge (Brown 1981; Rooker et al. 1998; van Montfrans et al., unpublished data). In most estuaries, larvae settle in seagrass beds and remain in these habitats as juveniles from late spring through summer (Chester and Thayer 1990; Rooker et al. 1998). In the Chesapeake Bay, sampling over the last seven years has shown that juveniles remained in these habitats for three to four months (van Montfrans et al., unpublished data) before leaving the Bay in the fall. As most seagrass beds in the Chesapeake Bay possess their own distinct chemical signatures (Chapter II), I could appropriately assume that otoliths of juvenile spotted seatrout caught in a seagrass bed carry geochemichal signatures of that specific bed.

Using juvenile spotted seatrout, I test the assumption that otoliths accurately record the chemistry of the inhabited habitats for [Mg/Ca], [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca]. I predict the relation between water chemistry and otolith microchemistry for these trace elements in the context of the physical and chemical processes that may regulate such relationships in Chesapeake Bay. In addition, observed patterns in otolith [Sr/Ca] were validated using otolith $\delta^{18}O$. This study is the first report of a field based-test of the relation between otolith and water chemistry in an estuary.

3.2. Methods

3.2.1. Model species and assumptions

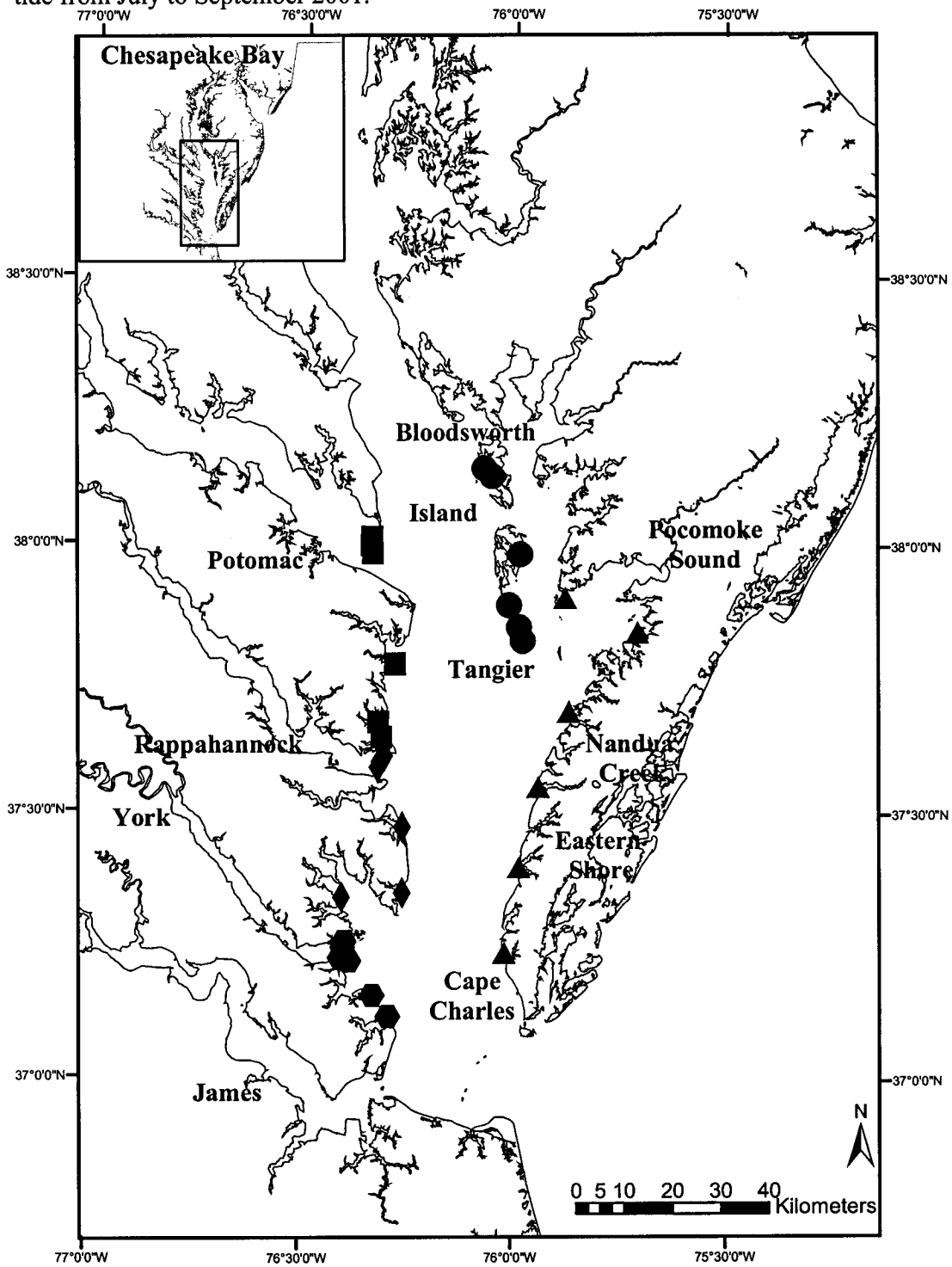
Juvenile spotted seatrout were collected in five seagrass habitats in the lower Chesapeake Bay: Potomac, Rappahannock, York, Island, and Pocomoke (Fig. 3.1). The Pocomoke habitat was located from the Pocomoke Sound to Nandua creek. Juvenile spotted seatrout are residents of these seagrass habitats from the early juvenile stage (11-40mm SL) to the late juvenile stage (140 mm) (Orth and Heck 1980; Brown 1981; Rooker et al. 1998). In this study, I included fish that had standard lengths between 20 and 70 mm. Thus, I limited collections to fish that had been exposed only to water chemistry of the seagrass habitats where they were captured.

In this context I further assumed that otolith chemistry of juvenile spotted seatrout reflected the variability in the chemistry of dissolved trace, minor, and major elements due to water composition, temperature, salinity, and pH of a given habitat. I also assumed that otolith microchemistry could be affected by physiological processes for those elements that are biologically mediated (e.g., Ca).

3.2.2. Water and fish collection

I sampled water and juvenile fish fortnightly in seagrass habitats of the Chesapeake Bay from July through September 2001 using a nested design with individual seagrass beds (stations) nested within habitat. At each station, water was collected using trace-elements clean procedures as described in Chapter II. Each water sample was taken using a peristaltic pump (Masterflex 7520-60) while being filtered through a Gelman® capsule (0.45 μm). Thus, only the dissolved colloidal fractions were retained

Fig. 3.1. Map of the lower Chesapeake Bay showing the locations of sampling habitats and stations. Five seagrass habitats were sampled for water and juvenile spotted seatrout: Potomac, Rappahannock, York, Island, and Pocomoke. At each station, water samples and juvenile fish were collected twice monthly during spring tide from July to September 2001.



(operationally defined as the dissolved load). Water samples were acidified to pH < 2 (using ultrapure HNO_3) and stored in Nalgene high-density-fluorinated bottles (Chapter II). All samples were chilled on ice in the field and refrigerated in the laboratory until analysis.

Juvenile spotted seatrout were randomly collected at each station (seagrass bed) using an otter trawl (0.64 cm stretched mesh, 7.9 m length). For each sampling day and station I made a minimum of three random tows. Each tow lasted two minutes and both location and distance covered were registered using a global positioning system (GPS). Fish captured in the same tow were stored in Ziploc® bags, labeled, and preserved on ice. In the laboratory, I recorded weight, standard and total lengths of each individual fish, and subsequently all fish were frozen. All fish caught in the Island, York, and Rappahannock habitats were used, but fish from the Potomac and the Pocomoke Sound habitats were more numerous and were randomly subsampled.

3.2.3. Trace element analysis in waters

Dissolved trace and minor elements in water were quantified using ICP-MS based on the method of external calibration with internal standardization (Chapter II; Taylor 2001). Indium (In) was used, as the internal standard, and each water sample was diluted five fold for a final solution of In 4 ppb. I measured the concentration of Mg, Ca, Mn, Sr, Ba, and La in each aliquot. Mg, Ca, Mn, Sr, and Ba were selected because they are commonly used in otolith microchemistry. Although in a laboratory experiment Ennevor and Beames (1993) demonstrated that La could be absorbed from water and deposited in otoliths, this element has not been previously used to study population structure and

environmental history of fish. The acquisition parameters, method detection limit (MDL), and precision (%RSD) for these six elements are reported in Table 3.1. Data were corrected for matrix effects and instrument drift, then the concentration of each element was determined from calibration curves established based on known concentration of the analytes in calibration standard solutions (Chapter II; Table 3.1).

3.2.4. Trace element analysis in otoliths

I extracted the sagittal otoliths from individual fish in a class-100 clean room using acid-washed glass probes. The right sagittal otolith was selected for solution based ICP-MS analysis, while the left otolith was used to determine $\delta^{18}O$ and $\delta^{13}C$.

Each sagittal otolith was cleaned with milli-Q water and all tissue was physically removed with acid-washed glass probes, then the otolith was soaked for five minutes in ultrapure hydrogen peroxide (33% H_2O_2) to remove all possible remnant tissues. Otoliths were rinsed three times with milli-Q water and dried under a positive flow hood, transferred to five mL of milli-Q water in acid-washed centrifuge-vials, sonicated for five minutes, and allowed to dry under a positive flow hood. Subsequently, all otoliths were weighed to the nearest 10 μg and dissolved in 100 μL of ultra-pure concentrated nitric acid, then made up to 1 mL with 900 μl of 1% ultrapure HNO_3.

Otoliths solutions were analyzed based on the same analytical procedure as for water (external standard with internal standardization) using a double focusing sector field inductively-coupled plasma mass spectrometer (Finningan MAT Element 2 ICP-MS). The internal standard used was In. Otolith solutions were sub-sampled and spiked with In, preparing aliquots of 1mL and 2 ppb In concentration. The aliquots were

Table 3.1. Summary of acquisition parameters, concentration of standards (low=L, medium= M, High= H), method detection limit (MDL), and mean estimates of precision (% RSD, relative standard deviation) from ICP-MS analysis of water samples collected in seagrass habitats of Chesapeake Bay from July to September 2001.

Isotopes	^{115}In	^{137}Ba	^{139}La	^{25}Mg	^{42}Ca	^{55}Mn	^{88}Sr	^{115}In
Concentration unit	ppb	ppb	ppt	ppm	ppm	ppt	ppb	ppb
Resolution	Low	Low	Low	Medium	Medium	Medium	Medium	Medium
Mass window	5	5	5	150	150	5	150	150
Settling time (ms)	0.0010	0.0010	0.0010	0.3000	0.001	0.0010	0.0010	0.3000
Sampling time (ms)	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200
Samples per peak	200	200	200	15	15	15	15	15
Method mass offset	0.0009	0.0002	0.0050	0.0011	0.0012	0.0007	-0.0001	0.0007
Standard (L)	4.0100	1.0200	2.0800	20.0700	20.4800	50.7900	39.9500	
Standard (M)	4.0100	10.0200	10.2500	106.0100	102.9900	250.6900	196.6100	
Standard (H)	4.0200	15.0600	20.5500	212.4900	206.2800	503.1800	397.6700	
MDL		0.0000	0.0110	0.0037	0.0000	5.0267	0.0260	
% RSD		1.1250	1.4500	3.9000	1.9000	1.8000	1.8500	

randomized within trays.

The six elements Mg, Ca, Mn, Sr, Ba, and La were also measured in otoliths. I summarized acquisition parameters, method detection limit (MDL), and precision (% RSD) for these elements in Table 3.2. RSD was estimated for each element based on repeated measurement of a quality control check standard (n= 30). Calibration procedures and correction for instrument drift and matrix effects were performed similarly to water analysis (Chapter II; Table 3.2). In particular, I was very conservative in estimating concentration of each analyte because I corrected for both analytical and procedural blanks. Further, all elements in both water and otoliths were normalized to Ca to allow comparison with other previously published studies.

3.2.5. Stable isotopes analysis of otoliths

The left sagittal otoliths were analyzed to determine oxygen and carbon isotopic composition using an automated Micromass IsoPrime carbonate analyzer at the Stable Isotope Laboratory (SIL) of the University of Maryland. Each otolith was ground into a fine powder, and 60-100 μg of otolith powder was sub-sampled for analysis. Both otolith and standard samples were spiked with 102% phosphoric acid at a temperature of 90 °C. $\delta^{18}O$ and $\delta^{13}C$ were measured based on the dual inlet method and coldfinger mode. Standards were prepared from limestone by Dr. A. J. Kaufman of the SIL of the University of Maryland. Ten otolith samples were sequentially analyzed after the measurement of five standard samples. After analysis the raw data was corrected and reported in ‰ –PDB (Peedee belemnite) using the standard δ notation. Precision of the measurements was 0.004 ‰ for $\delta^{13}C$ and 0.006 ‰ for $\delta^{18}O$ (average standard

Table 3.2. Summary of acquisition parameters, concentration of standards (low= L, medium= M, high= H), method detection limit (MDL), and mean estimates of precision (% RSD, relative standard deviation) from ICP-MS solution-based analysis of otoltihs of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay from July to September 2001.

Isotopes	^{25}Mg	^{55}Mn	^{115}In	^{137}Ba	^{139}La	^{42}Ca	^{88}Sr	^{115}In
Concentration unit	ppb	ppb		ppb	ppt	ppm	ppb	
Resolution	Low	Low	Low	Low	Low	Mediun	Mediun	Mediun
Mass window	5	5	5	5	5	150	150	150
Settling time (ms)	0.3	0.3	0.001	0.001	0.001	0.3	0.3	0.3000
Sampling time (ms)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.0200
Samples per peak	200	200	200	200	200	15	15	15
Method mass offset	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Standard (L)	10.03	4.05	2.03	2.05	10.35	50.01	103.88	
Standard (M)	50.15	20.32	2.03	10.17	51.46	249.68	504.18	
Standard (H)	100.19	40.57	2.03	20.4	102.41	499.12	1016.32	
MDL	0.009	0.012		0.0015	0.018	0.009	0.0465	
(% RSD)	0.7	0.6		1.4	1.4	6.6	1.8	

deviation of repeated measurements of the standards).

3.2.6. Statistical analysis

I used regression analyses to determine whether the ratios of metal to Ca (Me/Ca) and $\delta^{18}O$ measured in otoliths were related to otolith weight. Regressions were performed for each element and for the pooled data independently of seagrass habitats. When linear relationships were significant, I adjusted the concentrations as follow:

$$(1) \quad y_{i,adj} = y_i - bw_i$$

where, $y_{i,adj}$ is the adjusted concentration for the i^{th} otolith, y_i the original concentration of the i^{th} otolith, b the slope estimated from the regression, and w_i the weight of the i^{th} otolith.

Least squares methods were used to quantify the relation between trace-element chemistry in otoliths with either mean salinity or mean $[Me/Ca]_{water}$ within habitats as independent, fixed factors. Dependent variables were the mean $[Me/Ca]_{otolith}$, which were treated as random factors. Observations used to compute the mean $[Me/Ca]_{otolith}$ were tested for lack of linear fit with both independent variables (Appendix I). Subsequently I performed a weighted-regression analysis on the mean of $[Me/Ca]_{otolith}$ against mean salinity or mean $[Me/Ca]_{water}$ within habitats for variables showing no significant lack of linear fit. Weights were sample size divided by variance of $[Me/Ca]_{otolith}$ in a given habitat. A model was reported when the regression coefficient was different from 0. Also I used Spearman correlation to quantify monotonic behavior between the mean of $[Me/Ca]_{otolith}$ with salinity or $[Me/Ca]_{water}$.

Though this study was not designed to evaluate uptake of trace elements by

spotted seatrout, I estimated the partition coefficient of [Sr/Ca] in each habitat using the following equation.

$$(2) \qquad y = k_{dMe} * x$$

Where y is the mean of $[Me/Ca]_{otolith}$ in a given habitat, x the mean of $[Me/Ca]_{water}$, and k_{dMe} the distribution coefficient of the trace metal. This is an approximation of the equation used in Sholkovitz and Shen (1995) and Bath et al. (2000). The partition coefficient of [Sr/Ca] was determined along with the relationship between $[Sr/Ca]_{water}$ and $\delta^{18}O$ in otoliths to test whether concentration $[Sr/Ca]_{otolith}$ was influenced by temperature. Regressions of otolith $\delta^{18}O$ on water chemistry were based on the same statistical procedure for the trace elements. All regression analyses were done using NCSS 2001[3].

3.3. Results

3.3.1. Somatic characteristics of sampled juveniles

A total of 83 fish were used in the study, with the smallest measuring 15.7 mm (SL) and the largest 64.29 mm (SL) (Figure 3.2). About 90% of the juveniles had an otolith weight below 3 g (Fig. 3.3), thus allowing comparison to results from laboratory experiments (e.g., Bath et al. 2000, Fowler et al. 1995, Milton and Chenery 2001).

Otolith weight was not significantly different among habitats ($p = 0.12$; Power= 0.53). Regression and correlation of otolith microchemistry and otolith weight (w) were significant only for [Mg/Ca] and $\delta^{18}O$ (Figure 3.4) following the equations below:

$$(1) \qquad [Mg/Ca]_{otolith}\ (\mu mol/mol) = -0.026 * w + 0.34 \ (r^2 = 0.83, n = 81).$$

[3] NCSS 2001. Number Cruncher Statistical System. Released by Dr Jerry L. Hintze. 329 North East Kaysville, Utah 84037.

Fig. 3.2. Frequency distribution of standard length (mm) of juvenile spotted collected in seagrass habitats of Chesapeake Bay in 2001. Total sample size, $n = 83$.

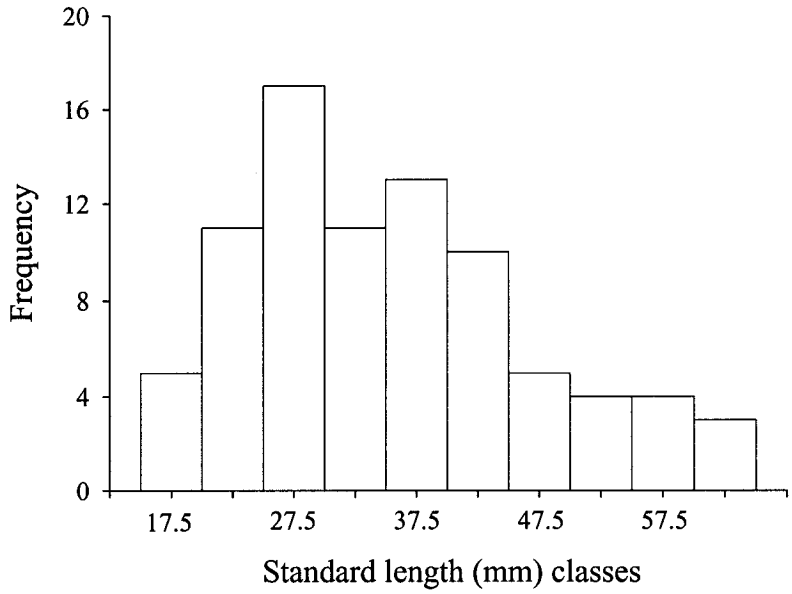


Fig. 3.3. Relationship between otolith weight and standard length (mm) of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay in 2001. Total sample size, $n = 83$.

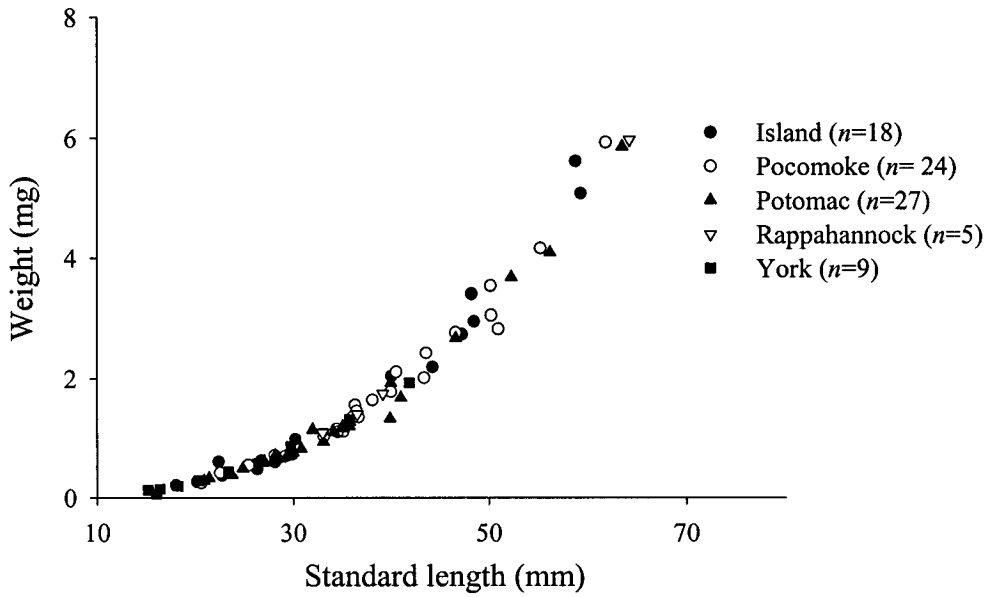
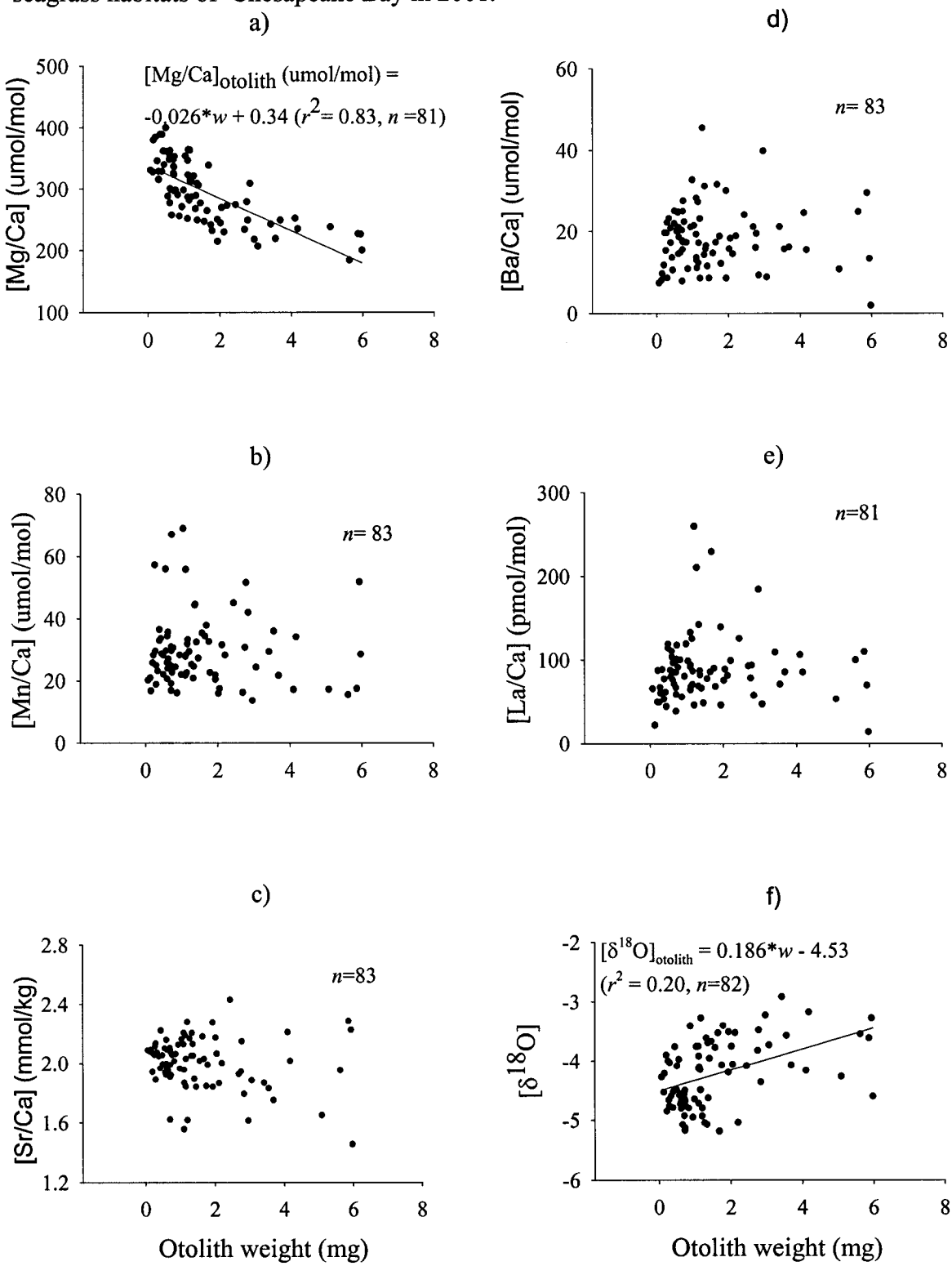


Fig. 3.4. Regression of otolith weight (mg) against trace-element concentration and [$\delta^{18}O$] measured in otoliths of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay in 2001.



(2) $[\delta^{18}O]_{otolith} = 0.186*w - 4.53$ (r^2=0.20, n=83).

3.3.2. $[Me/Ca]_{otolith}$ versus salinity

Salinity within each habitat varied little during the sampling period (Chapter II) but was significantly different among habitats (Table 3.3). However there was no significant difference between the Island and the Potomac habitats and between the Pocomoke and the Rappahannock habitats. This pattern of variability in salinity provided an ideal test to determine whether fish that have experienced similar levels of salinity would have similar levels of $[Me/Ca]_{otolith}$, while contrasting the effect of salinity on $[Me/Ca]_{otolith}$ among habitats along the estuary.

Otolith [Ba/Ca] and [La/Ca] were not significantly different in habitats that had similar salinity concentration across the lower Chesapeake Bay (Fig. 3.5). However, $[Ba/Ca]_{otolith}$ and $[La/Ca]_{otolith}$ showed significant difference among habitats along the longitudinal gradient from North to South. The mean of the ratios of $[Ba/Ca]_{otoltih}$ estimated in seagrass habitats decreased with increasing salinity (Fig. 3.5d). This relation was linear and the weighted regression explained 92% of the variation (Table 3.4). The model can be described as follows:

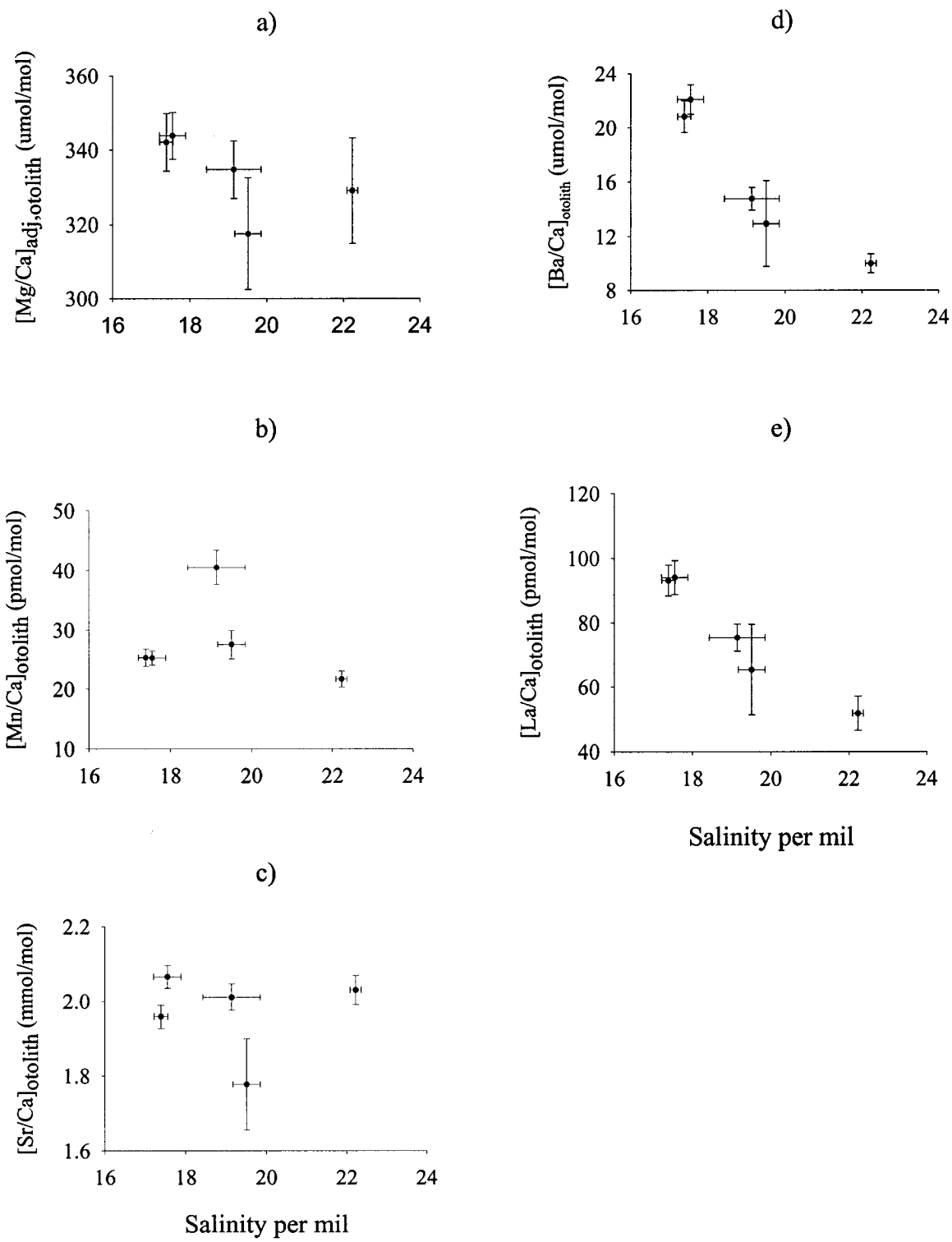
(3) $[Ba/Ca]_{otolith}$ (μmol/mol) = -2.28± 1.26 * (salinity) + 60.13 ± 24.09 (95% confidence interval).

These results were consistent with observed depletion of Ba along the salinity gradient in Chesapeake Bay from July to September (Chapter II). Thus, otolith microchemistry

Table 3.3. Mean estimates of salinity measured in water samples collected in seagrass habitats of Chesapeake Bay from July to September 2001.

Habitats	Mean	Standard Error	*n*
Island	17.39	0.17	35
Pocomoke	19.14	0.17	18
Potomac	17.55	0.34	21
Rappahannock	19.51	0.34	20
York	22.23	0.14	21

Fig. 3.5. Effect of salinity on the concentration of [Mg/Ca], [Mn/Ca], [Sr/Ca], [Ba/Ca] , and [La/Ca] measured in otoliths of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay from July to September 2001. Bars are standard errors of the mean values. Note that adj = adjusted value for otolith weight.



could be predicted when average salinity in a given habitat is known over the period of residence of juvenile spotted seatrout in seagrasses. These results showed that very small changes in salinity may result in significant differences in $[Ba/Ca]_{otolith}$ within the estuary.

Similarly, $[La/Ca]_{otolith}$ was highly and negatively correlated with salinity (Fig. 3.5e). The relation was strongly linear with a weighted regression that explained 98 % of the variability.

(4) $[La/Ca]_{otolith}$ (pmol/mol) = $-8.82 \pm 2.31 * (\text{salinity}) + 246.36 \pm 44.09$

(95% confidence interval).

These patterns reflected the removal of light rare earth elements (LREE: La to Nd) from solution with increasing salinity, which is typical in estuarine waters and particularly in Chesapeake Bay (Sholkovitz and Elderfield et al. 1988; Dorval et al. 2001). Salinity appears to be an excellent predictor of $[La/Ca]_{otolith}$ between habitats in the Bay. In addition, as La is highly correlated to the other REEs, it can be inferred that salinity might predict otolith concentration of both LREE and heavy REEs (HREE: Tb to Lu).

Though the relation between $[Mg/Ca]_{adj,otolith}$ and salinity was linear, the regression and correlation coefficients were not significant (Table 3.4). As Mg is conservative in surface waters of the Chesapeake Bay and exhibits increased concentration with increasing salinity from July to September (Chapter II), it is likely that juvenile spotted seatrout may strongly regulate the concentration of Mg in their blood plasma. These results were consistent with the expected behavior of Mg in most fish species (e.g., Campana 1999). However, within habitat variability of $[Mg/Ca]_{adj,otolith}$ was higher than the other trace elements (Fig. 3.5a), which might indicate more sensitivity of Mg to sample size or instability in the aragonite lattice (Amiel et al. 1973, Mitsugushi et

Table 3.4. Results of the quantification of the relationship between juvenile spotted seatrout-otolith and surface-water chemistry.

Relationship	Linear fit		Weighted regression		Spearman correlation	
	Tdf	Stat. significance	r^2	Stat. significance	r	Stat. significance
$[Mg/Ca]_{adj,otolith}$ vs salinity	80	0.7046 NS	0.582	0.133 NS	-0.732	0.160 NS
$[MnCa]_{otolith}$ vs salinity	82	0.0000 S				
$[Sr/Ca]_{otolith}$ vs salinity	82	0.0028 S				
$[Ba/Ca]_{otolith}$ vs salinity	79	0.0650 NS	0.923	0.009 S	-0.9314	0.021 S
$[La/Ca]_{otolith}$ vs salinity	74	0.7429 NS	0.980	0.001 S	-0.8806	0.000 S
$[Mg/Ca]_{otolith}$ vs $[Mg/Ca]_{water}$	80	0.2520 NS	0.442	0.442 NS	-0.6146	0.270 NS
$[Mn/Ca]_{otolith}$ vs $[Mn/Ca]_{water}$	82	0.0083 S				
$[Sr/Ca]_{otolith}$ vs $[Sr/Ca]_{water}$	82	0.0080 S				
$[Ba/Ca]_{otolith}$ vs $[Ba/Ca]_{water}$	79	0.0000 S				
$[La/Ca]_{otolith}$ vs $[La/Ca]_{water}$	74	0.0003 S				
$[\delta^{18}O]_{adj,otolith}$ vs salinity	73	0.0002 S				
$[\delta^{18}O]_{adj,otolith}$ vs $[Sr/Ca]_{otolith}$	73	0.0000 S				
$[\delta^{18}O]_{adj,otolith}$ vs $[Sr/Ca]_{water}$	73	0.3066 NS	0.983	0.001 S	0.9554	0.011 S
$[\delta^{18}O]_{adj,otolith}$ vs k_{dSr}	73	0.0001 S				

Note: Water and juvenile fish were sampled in seagrass habitats of Chesapeake Bay from July to September 2001. Lack of linear fit tests were performed using [Me/Ca] of all otolith samples observed in a given habitat against mean salinity or mean $[Me/Ca]_{water}$ of this habitat. Weighted regressions were based on mean $[Me/Ca]_{otolith}$ against mean salinity or mean $[Me/Ca]_{water}$ in each habitat. Tdf= total degree of freedom, Stat. = statistical, NS = not significantly different, S= significantly different, and adj = adjusted value for otolith weight.

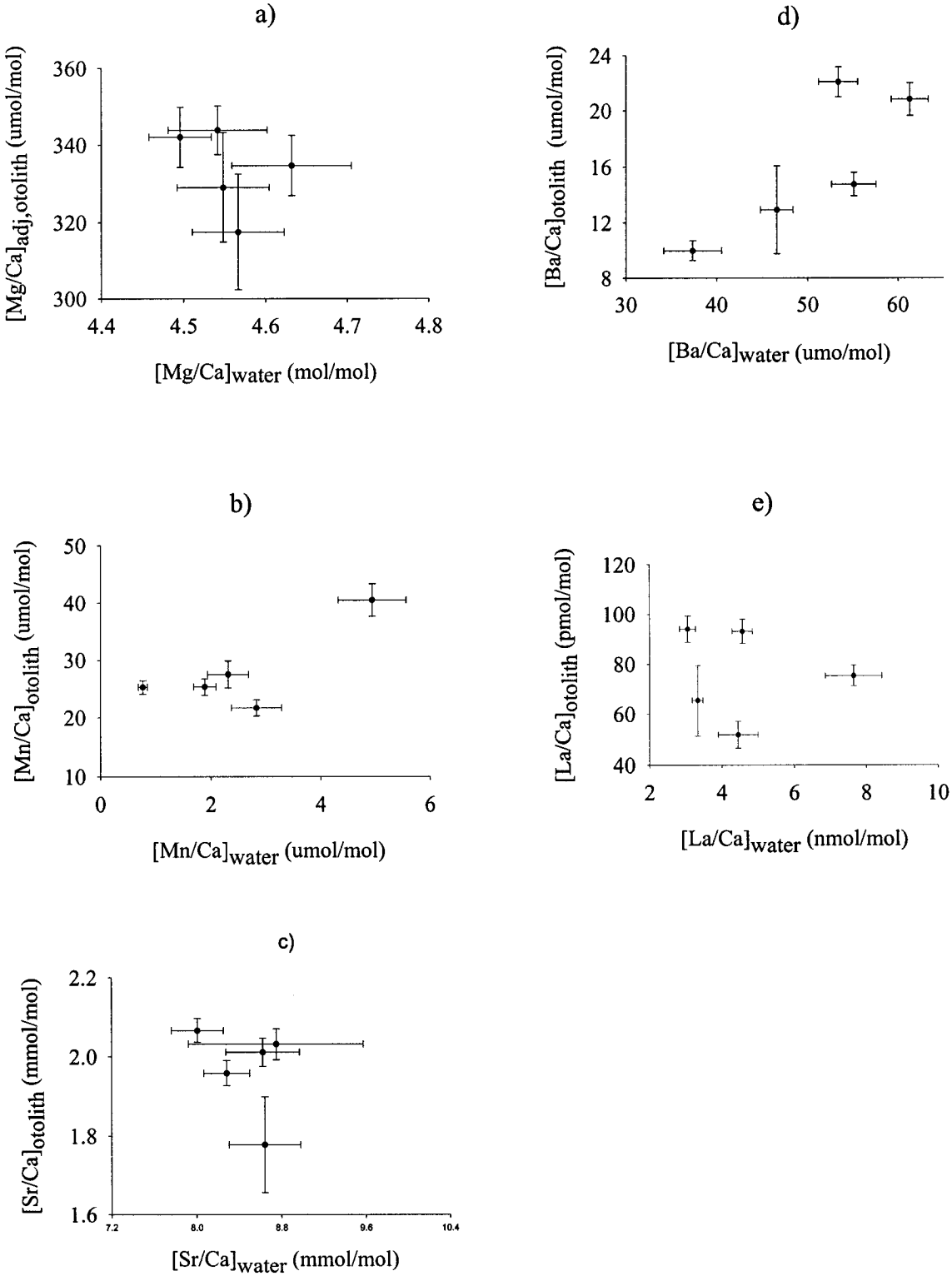
al. 1996).

Both $[Mn/Ca]_{otolith}$ and $[Sr/Ca]_{otolith}$ relations with salinity deviated from linearity (Fig. 3.5b, 3.5c). This pattern was anticipated for $[Mn/Ca]_{otolith}$ because Mn is a non-conservative element in Chesapeake Bay. Likewise its concentration is regulated by redox reactions rather than by physical mixing (Eaton 1979; Sholkovitz et a.1992). In contrast, the lack of $[Sr/Ca]_{otolith}$ relation to salinity was not expected, as previous authors have observed increases of $[Sr/Ca]_{otolith}$ with increasing salinity (e.g Fowler et 1995; Secor et al. 1995; Martin et al. in press). However, Fowler et al. (1995) pointed out that the effect of salinity was relatively small when compared to temperature. This means that the lack of linearity might be due to the effect of factors other than salinity such as temperature-degree days because of age difference among individual fish.

3.3.3. $[Me/Ca]_{otolith}$ versus $[Me/Ca]_{water}$

$[Ba/Ca]_{otolith}$ ratios were positively correlated with $[Ba/Ca]_{water}$ (Fig. 3.6d), but this relation was not linear (Table 3.4). Although the monotonic behavior agreed with that of Bath et al. (2000) and Milton and Chenery (2001), a linear model was not suitable to fit the data as was determined experimentally by those two authors. The lack of linearity resulted mostly from fish caught in the Pocomoke habitat. The $[Ba/Ca]_{otolith}$ in these fish was different from fish in the Island and Potomac habitats, whereas the difference in the ratios of [Ba/Ca] in surface waters of these three habitats was less pronounced. Except for the Pocomoke habitat, which is the only habitat that is not influenced by major freshwater input, linearity was preserved. It is likely that other chemical processes might have interacted with Ba uptake in otoliths within the Pocomoke habitat.

Fig. 3.6. Relationship between water and otolith chemistry for [Mg/Ca], [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca]. Fish and water samples were collected in seagrass habitats of Chesapeake Bay from July to September 2001. Bars are standard errors of the mean values. Note that adj = adjusted value for otolith weight.



There was no linear relation and no correlation between $[La/Ca]_{water}$ and $[La/Ca]_{otolith}$ (Table 3.3, Fig.3.6e). These results suggest that concentration of $[La/Ca]_{otolith}$ may be best predicted by salinity rather than by the concentration of this ratio in water of the seagrass habitats.

$[Mn/Ca]_{otolith}$ increased with increasing $[Mn/Ca]_{water}$ (Fig. 3.6b), but with no linearity (Table 3.3). Again this was mostly due to the Pocomoke habitat where [Mn/Ca] concentration in both waters and otoliths was nearly double the average of the others habitats. The other four habitats formed a well-defined cluster with little variability in their $[Mn/Ca]_{otolith}$ (Fig. 3.6b). Campana (1999) suggested that Mn in otoliths may not be biologically controlled. Thus, the $[Mn/Ca]_{otolith}$ from the Pocomoke fish may be directly related to water concentration. These spatial patterns may have resulted from differences in the magnitude of redox reactions that regulate Mn in Chesapeake Bay during summer (Eaton 1979; Sholkovitz et 1992).

The relation between $[Mg/Ca]_{adj,otolith}$ and $[Mg/Ca]_{water}$ was linear, but the regression and correlation coefficients were not significantly different from 0 (Table 3.4, Fig. 3.6a). These results retained the observed patterns with salinity and showed that juvenile spotted seatrout strongly regulate uptake of Mg from water.

The relation between $[Sr/Ca]_{otolith}$ and $[Sr/Ca]_{water}$ (Fig. 3.6c) departed strongly from the positive and linear relation predicted in Bath et al. (2000) and Milton and Chenery (2001). Because there was no significant variation of temperature among habitats (Chapter II) during the sampling period, I could not explain these differences as direct temperature effects (cf. Bath et al. 2000). However, as temperature fluctuated, from an overall mean of 25.66 °C in July to 27.4 °C in August and 23.1°C in September

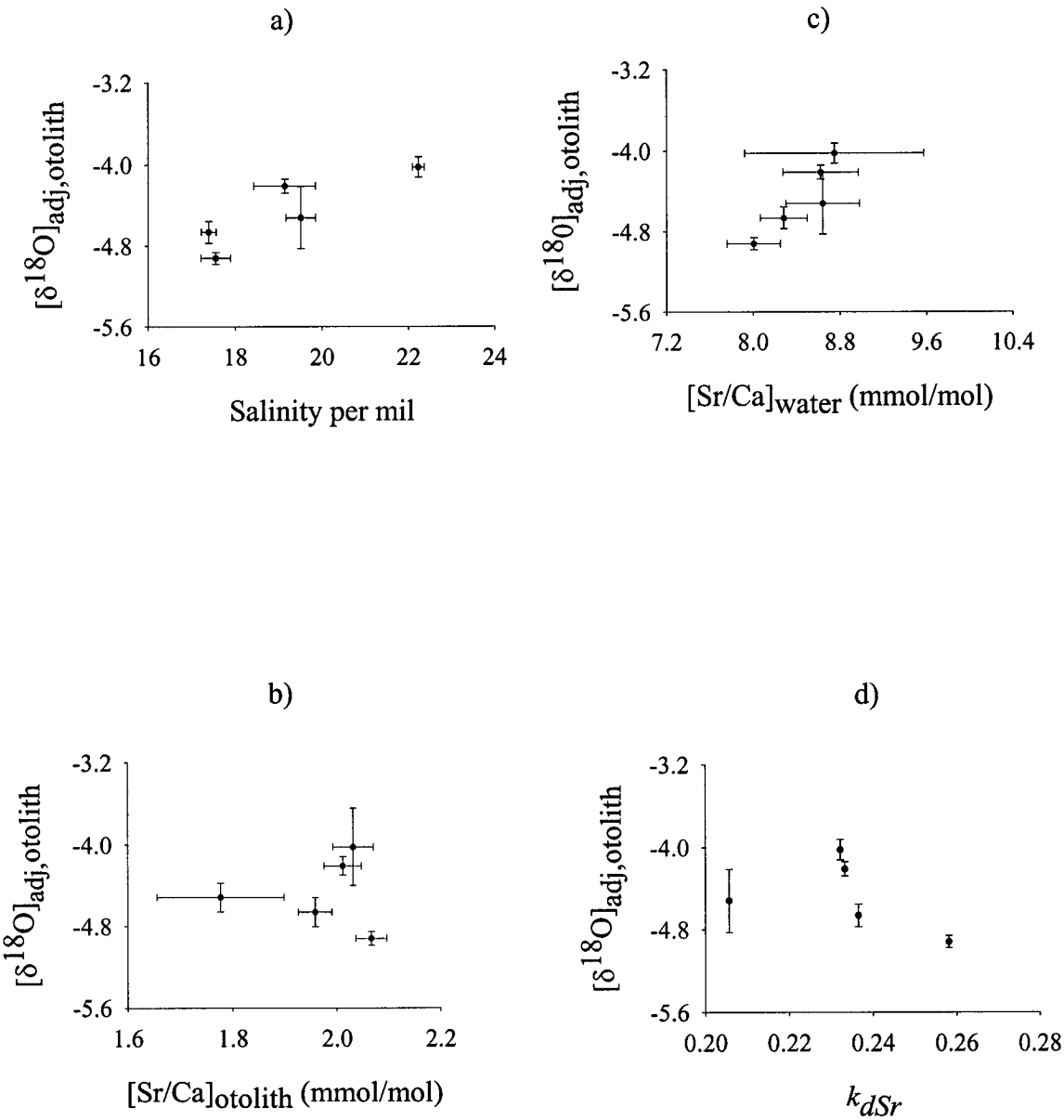
(Chapter II), the cumulative effect of temperature over time might have caused the deviation from linearity. I hypothesized that if the cumulative change in temperature did alter the $[Sr/Ca]_{otolith}$, either $[Sr/Ca]_{otolith}$ or its partition coefficient (k_{dSr}) in each habitat would be highly correlated to any variables that could represent the influence of temperature over time.

I tested this hypothesis by comparing the $[Sr/Ca]_{otolith}$ to $\delta^{18}O_{adj,otolith}$ which could represent the integrated temperature effect, because otolith $\delta^{18}O$ is highly and negatively correlated with temperature (e.g., Kalish 1991a, 1991b; Radtke et al. 1996), and in this study I adjusted otolith $\delta^{18}O$ so that it is neither age nor weight dependent, assuming older fish have larger otoliths. This is a very reasonable assumption as the relation between age and length is expected to be linear for juvenile spotted seatrout (McMichael and Peters 1989; Murphy and McMichael 2003). In addition Bath et al. (2000) showed that $[Sr/Ca]_{otolith}$ did not vary with growth rate, and similarly in this study I found no significant relation between $[Sr/Ca]_{otolith}$ and otolith weight. Nevertheless, $\delta^{18}O_{adj,otolith}$ did not show a linear relation with either $[Sr/Ca]_{otolith}$ or k_{dSr} (Table 3.4, Fig. 3.7b, 3.7d). Moreover, the isotopic composition of oxygen was correlated with salinity and $[Sr/Ca]_{water}$ (Fig. 3.7a, 3.7c). There was a linear and predictive relation between $\delta^{18}O_{adj,otolith}$ and $[Sr/Ca]_{water}$ (Table 3.4), which can be described based on the weighted regression as:

(5) $[\delta^{18}O]_{adj,otolith} = 1.168 \pm 0.406 * [Sr/Ca]_{water}$ (mmol/mol) -14.286 ± 3.674 (95% confidence interval).

These results provide strong evidence that $[Sr/Ca]_{otolith}$ and $[Sr/Ca]_{water}$ are

Fig. 3.7. Mean [$\delta^{18}O$] measured in otoliths of juvenile spotted seatrout plotted against the mean of salinity, $[Sr/Ca]_{otolith}$, $[Sr/Ca]_{water}$, and k_{dSr}. Fish and water samples were collected in seagrass habitats of Chesapeake Bay from July to September 2001. Bars are standard errors of the mean values. Note that adj = adjusted value for otolith weight.



decoupled. Therefore, $[Sr/Ca]_{otolith}$ of juvenile spotted seatrout residing in seagrass habitats of the lower Chesapeake Bay, may not be a simple linear function of water concentration and ambient temperature as predicted by Bath et al. (2000).

3.4. Discussion

Mixing processes and salinity exerted control on $[Ba/Ca]_{otolith}$ in fish caught in seagrass habitats in Chesapeake Bay. The relation of $[Ba/Ca]_{otolith}$ with salinity was inversely linear. The model reflected the conservative behavior of Ba in the lower Chesapeake Bay, where Ba decreases with increasing salinity within and across months from July to September. This distribution of Ba is typical in estuaries when there is no significant input from biological activity in the water column (e.g., Zwolsman and van Eck 1999). However, the relation of $[Ba/Ca]_{otolith}$ and $[Ba/Ca]_{water}$ was non linear and depended on the geographic location of the habitats. Thus, the linear relation predicted by Bath et al. (2000) and Milton and Chenery (2001) did not hold in this first field test and was mostly due to the behavior of [Ba/Ca] in the Pocomoke habitat. Among the five habitats studied, the Pocomoke Sound is the only one that is not directly influenced by a major tributary. More replications of this study are needed to determine whether the concentration of $[Ba/Ca]_{otolith}$ in the Pocomoke habitat results from physical and chemical processes that control the concentration of this ratio in water and otoliths. Nevertheless, in the Chesapeake Bay salinity appears to be the chief regulator of the concentration of [Ba/Ca] in otoliths of fish caught in the seagrass habitats.

$[La/Ca]_{otolith}$ varied with salinity similarly to $[Ba/Ca]_{otolith}$, but $[La/Ca]_{otolith}$ patterns resulted from different physical and chemical processes. First, the decrease of

dissolved La from low to high salinity is regulated by colloidal complexation reactions and adsorption onto particles (Sholkovitz and Elderfield 1988). At low pH, LREEs such as La are preferentially removed from solution, relative to HREEs, by dissolved particulate matter, with most of this fractionation occurring during early estuarine mixing. In addition, colloidal complexation of REEs increases with salinity in the mixing zone, leading to further removal of these elements from the water column (e.g., Sholkovitz and Elderfield 1988; Elderfield et al. 1990; Dorval et al. 2001). In seawater, $LaCO_3$ is the most abundant species of La and as much as 86% of La may be complexed in this form (e.g., Cantrell and Byrne 1987). Likewise, fish from higher salinity habitats had lower $[La/Ca]_{otolith}$ because of higher removal of La in surface waters (Millero 1992; Bertine et al. 1996) by carbonate at lower salinity. Accordingly, my results show that in the lower Chesapeake Bay, there might still be further removal of LREEs by carbonate complexation along the seagrass habitats whose salinity varies from 17 to 23 ppt. Second, though the otolith microchemistry of Ba and La does have some similarities, they differ greatly. Indeed, neither La nor Ba is biologically controlled and therefore it is more likely that their composition in water would predict their concentration in the otoliths. However, the bulk of incorporation of Ba^{+2} in otoliths is achieved through substitution to Ca^{+2} or coprecipitation in the crystalline matrix because these elements have the same valence and close ionic radii (Campana 1999; Milton and Chenery 2001). In contrast, La is a trivalent element with a different ionic radius than Ca. Therefore La^{+3} mostly occurs within the spaces of the aragonite lattice (Fritz et al. 1990, Geffen et al. 1998). The differences between the REEs and other trace metals confer on them unique properties useful in identifying habitat to small-spatial scale.

The ratio of $[Mn/Ca]_{otolith}$ showed no linear relation with either salinity or $[Mn/Ca]_{water}$, though it was positively correlated with the $[Mn/Ca]_{water}$. These patterns were tied to the non-conservative behavior of Mn (Eaton 1979; Sholkovitz et al. 1992) in Chesapeake Bay waters, but also may result from the fact that Mn in fish otoliths may not be physiologically controlled. Concentration of Mn in the water column of the Chesapeake Bay peaks during summer time when anoxic conditions dominate in deep bottom water and in surface sediment (Eaton 1979; Sholkovitz et al. 1992). Consequently, variation of [Mn/Ca] is not coupled to the magnitude of freshwater input from the major tributaries. Although, using limited data, Campana (1999) suggested that Mn is among the trace elements whose uptake in otoliths is not likely to be regulated to any significant extent; therefore fish otoliths are more likely to reflect water concentration in Mn. Interestingly, these factors led to heterogeneous distribution of Mn in both water and otoliths in my field study, leading to the separation of the Potomac habitat from the other seagrass habitats. These findings show clearly that the chemical processes acting on very small spatial scales in the Bay may confer to $[Mn/Ca]_{otolith}$ unique characteristics making it a potential habitat-specific biogeochemical marker.

The relation of $[Mg/Ca]_{otolith}$ to $[Mg/Ca]_{water}$ chemistry was as expected. Fowler et al. (1995) observed a negative correlation with salinity, whereas in foraminiferal calcite Nurnberg et al. (1996) observed a positive correlation. The decoupling of $[Mg/Ca]_{otolith}$ with $[Mg/Ca]_{water}$ suggests that juvenile spotted seatrout strongly regulate Mg concentration in their blood plasma (Campana 1999, Evans 1993). However, Mitsugushi et al. (1996) pointed out that the location of Mg^{2+} in coral aragonite crystal is not well understood, and it may be weakly bound to the lattice due to its small ionic

radius. In addition, Amiel et al. (1973) observed that in coral aragonite Mg was preferentially released from the lattice to distilled water. This suggests that Mg may also leach out of otoliths, rendering its concentration more variable relative to other elements. Therefore, $[Mg/Ca]_{otolith}$ is likely to be unstable, and may not constitute a reliable tracer to identify habitat use by fish.

The uptake of $[Sr/Ca]_{otolith}$ by juvenile spotted seatrout contrasted with results from recent laboratory studies. In the lower Bay, I found no obvious relation of $[Sr/Ca]_{otolith}$ to either salinity or $[Sr/Ca]_{water}$. First, this is contrary to the positive correlation with salinity reported by Fowler et al. (1995), Secor et al.(1995) and Martin et al. (In press) in the laboratory. Second, $[Sr/Ca]_{otolith}$ and $[Sr/Ca]_{water}$ relationship in this study deviated from the linear relation predicted by Bath et al. (2000) and by Milton and Chenery (2001). Based on the distribution coefficients estimated for [Sr/Ca] and $[\delta^{18}O]_{otolith}$, I found no evidence that $[Sr/Ca]_{otolith}$ was directly affected by temperature. In that respect, these results were consistent with Kalish (1989), who found no evidence for a linear relation between otolith [Sr/Ca] and temperature in Australian salmon raised in laboratory. However, these results are not yet conclusive because it is likely that observed concentration of $[Sr/Ca]_{otolith}$ may have resulted from the effect of temperature-degree days. Because juvenile spotted seatrout used in this study were not of the same age, they had been exposed to different lifetime temperature. Thus, degree-day temperature exposure may have confounded the effect of salinity or $[Sr/Ca]_{water}$ on $[Sr/Ca]_{otolith}$. In this context, an unequivocal understanding of the factors controlling $[Sr/Ca]_{otolith}$ in juvenile spotted seatrout awaits the determination of age and lifetime temperature exposure for each individual fish.

An important finding of this study was the positive correlation between otolith $\delta^{18}O$ with both salinity and $[Sr/Ca]_{water}$. Many studies have observed the relation between seawater $\delta^{18}O$ and $[Sr/Ca]_{water}$, but direct correlation of otolith $\delta^{18}O$ to $[Sr/Ca]_{water}$ in an estuary had not been reported before. These results showed that $[Sr/Ca]_{water}$ might be used as a proxy for the oxygen isotopic composition of otoliths in the lower Chesapeake Bay. In addition, several studies have demonstrated that $\delta^{18}O$ is accumulated in otolith under near equilibrium making it a reliable indicator of ambient temperature (Kalish 1991a, Kalish 1991b; Radtke et al.1996; Thorrold 1997b; Høie et al. 2003). Though I did not measure $\delta^{18}O$ in the water, the relation between otolith $\delta^{18}O$ with $[Sr/Ca]_{water}$ indicates that $\delta^{18}O$ in the water may also constitute a useful tracer of the ambient environment in seagrass habitats.

In an estuary such as the Chesapeake Bay, water chemistry will be predictive of otolith microchemistry only for trace elements that are not directly or indirectly biologically mediated and that are not sensitive to temperature, such as Ba and La. However, though water chemistry may be predictive of [Ba/Ca] and [La/Ca] in otoliths along the estuary, it may not be a good predictor to locate individual fish laterally across the lower Chesapeake Bay. In small and narrow estuaries dominated by one river system (e.g., Hudson River), dissolved Ba and La may be used as a surrogate to predict otolith microchemistry. In wide estuaries, having different rivers with varying freshwater input, analysis of water chemistry variations may not be powerful enough to predict otolith microchemistry, especially in detecting differences laterally. In such conditions, a library of juvenile otoliths is required to study population dynamics and life history of fish living in such environments. The need for an otolith library is further emphasized because

extrapolation of expected otolith trace-element composition from laboratory experiments might significantly depart from that observed in wild-caught fish.

These findings have important implications for the future management of seagrass habitats in Chesapeake Bay. First, they show that resident fish have experienced different water-mass exposure, and this different exposure is clearly reflected in the otolith trace elements, such as Mn, Ba, and La. Second, resident fish in the Island habitat had significantly different chemistry from those in the Pocomoke habitat. These results show that small-scale spatial variations in the Bay are resolvable based on water chemistry and otolith microchemistry. Finally, juvenile otoliths can be used as a natural tag to study dynamics of spotted seatrout within the Chesapeake Bay. As submerged aquatic vegetations are declining in the Bay (Orth and Moore 1983), otolith chemistry may potentially lead to the determination of habitat-specific survivorship and thus identify the most important seagrass habitats to preserve.

3.5. Conclusion

Using juvenile spotted seatrout as model species I tested the hypothesis that otoliths accurately record the water chemistry of five seagrass habitats in Chesapeake Bay. I found that there was predictive relation for elements that are not physiologically controlled and that are not sensitive to temperature such as [Ba/Ca] and [La/Ca]. Salinity was the best predictor for both [Ba/Ca] and [La/Ca] in otoliths. There was a positive correlation between $[Ba/Ca]_{otolith}$ and $[Ba/Ca]_{water}$, but the relation was not linear as previously found in laboratory experiments. As expected $[Mg/Ca]_{otolith}$ did not correlate to $[Mg/Ca]_{water}$, and thus this ratio is not likely to be a reliable tracer to identify habitat

use by fish. Contrary to expectation $[Sr/Ca]_{otolith}$ was decoupled with water chemistry, which suggests that concentration of $[Sr/Ca]_{otolith}$ may not be a simple function of salinity and $[Sr/Ca]_{water}$. However, there was a predictive relation between $[\delta^{18}O]_{otolith}$ and $[Sr/Ca]_{water}$, showing that $[\delta^{18}O]_{otolith}$ may be a useful tracer of ambient water in the seagrass habitats. The Pocomoke habitat was separated from all other habitats based on [Mn/Ca] in water and otoliths. This confers to otolith Mn unique characteristics to be a habitat-specific biogeochemical marker. Finally, I determined that water chemistry could not be used as surrogate for otolith microchemistry in wide estuaries, and therefore a library of juvenile otoliths is required to study life history and dynamics in such systems.

CHAPTER IV

OTOLITH MICROCHEMISTRY MAY BE USED TO IDENTIFY ESSENTIAL SEAGRASS HABITATS FOR JUVENILE SPOTTED SEATROUT, *CYNOSCION NEBULOSUS*, IN CHESAPEAKE BAY

4.1. Introduction

The loss of seagrass habitat in estuaries is a major threat to the sustainable exploitation and conservation of fish populations (Rajasuriya 1996; Patillo et al. 1997; Bunting 2001). Seagrass beds are primary nursery habitats for juveniles of estuarine-dependent fish (Bell and Pollard 1989; Sogard and Able 1991; Hannan and Williams 1998). These habitats provide shelter from predation and abundant food to juvenile fish (Orth et al. 1984; Rozas and Odum 1988; Heck and Crowder 1991), influencing their vital rates, such as growth and mortality (Jenkins et al. 1993; Rooker et al. 1999; Stunz et al. 2002). Consequently, the decline of seagrasses may reduce the fitness of inhabiting populations, and thus threaten their persistence over time. Such a negative effect may be exacerbated for fish populations that are heavily exploited. Spotted seatrout, *Cysnoscion nebulosus*, is one such species whose population decline has been hypothesized to result from both overfishing and loss of habitat in estuaries (Patillo et al. 1997; Gold et al. 2003).

As in most estuaries, spotted seatrout are locally adapted to seagrasses in the Chesapeake Bay (Brown 1981; McMichael and Peters 1989; Chester and Thayer 1990; Rooker et al. 1998). Spotted seatrout post-larvae settle in seagrasses and remain in these habitats until the late-juvenile stage, spanning generally a period of three to four months

from late spring to early fall (Brown 1981; Orth and Heck 1980; Rooker et al. 1998, van Montfrans et al., unpublished data). The Chesapeake Bay population is genetically separated from other populations along the U.S Atlantic East Coast (Wiley and Chapman 2003), and differs from others because it is the only known spotted seatrout population that undergoes extensive fall and spring migration. Young-of-the year and adult fish leave the Bay in the fall and migrate to southern feeding grounds, returning in late spring to spawn during peak abundance of food in seagrasses (Livingston 1984). Therefore, recruitment of this population depends critically on the health of the seagrass habitats in the Chesapeake Bay.

Seagrasses declined in the Bay throughout the 1970's reaching a low in 1984 (Orth and Moore 1983, Orth et al. 1998). Despite partial recovery in the 1990's, segrasses remain below historical levels and continue to decrease in the most important nursery habitats of juvenile spotted seatrout (Moore et al. 2000). This loss of habitat may affect the recruitment of spotted seatrout resulting in the decrease of population size as previously observed in other estuaries (Patillo et al. 1997, Gold et al. 2003).

Recent restoration efforts in the Bay have mostly focused on improving water quality by determining habitat requirements for aquatic vegetation (Dennison et al. 1993), while restoring seagrasses in areas of dramatic declines (Orth et al. 1994, Orth et al. 1999). Although these approaches (i.e., Orth et al. 1994, Orth et al. 1999) are promising, it is cost prohibitive to attempt to restore all seagrass habitats in the Bay. Moreover, seagrass-bed size does not account for variation in the abundance of fish associated with seagrasses (Bell et al. 2001), and cumulative mortality rates may preclude direct correlation between juvenile abundances and subsequent recruitment. In this context,

conservation would be more effective by targeting source-habitats that contribute most recruits to adult populations, rather than restoring sink-habitats that may lead to production of juvenile biomass but to few recruits.

The delineation of source-habitats requires methods that can identify natal habitats for each cohort of spotted seatrout. Application of artificial tags is the traditional method of identifying natal habitats and subsequent philopatry. This method cannot be applied to late-larvae and early-juveniles because of difficulties in tagging such small fish, sensitivity to sample size and inaccuracy of tag-derived estimates when mortality rate is high. Otolith microchemistry is an alternative method to determine natal habitat and philopatry in the Bay (Thorrold et al. 2001). Otolith microchemistry has been recently used to differentiate stocks and to reconstruct the life and environmental history of fish populations (Radtke et al. 1989, Edmond et al. 1992; Thresher et al. 1994; Radtke et al.1996, Begg et al. 1998). Recent studies have shown that trace-element and stable isotopic composition of otoliths are powerful tracers of water masses that can be used to determine natal origin of fish populations at large spatial scale between estuaries (Gillanders 2002, Thorrold 1998, Thorrold et al. 2001), and small spatial scale between sites within estuaries (e.g., Thorrold et al.1998, Gillanders and Kingsford 2000, Gillanders 2002, Secor et al. 2001). Additionally, this technique allows the study of dispersal rates within an estuary (Kimura et al. 2001). I have previously shown that surface-water chemistry in the lower Chesapeake Bay is significantly different among seagrass habitats, and also that concentrations of Mn, Ba, La, and $\delta^{18}O$ in otoliths reflect ambient water chemistry. Therefore, there may be sufficient differences in chemical signatures imparted to otoliths to identify natal habitats of juvenile spotted seatrout.

The purpose of this study was to determine whether otolith microchemistry could be used to identify the natal seagrass habitats for juvenile spotted seatrout. Specifically, I first compared the otolith microchemistry of juveniles caught in seagrass habitats within and between two years, and secondly, I assessed whether elemental and isotopic composition in otoliths could identify the natal habitat at fine spatial scale.

4.2. Methods

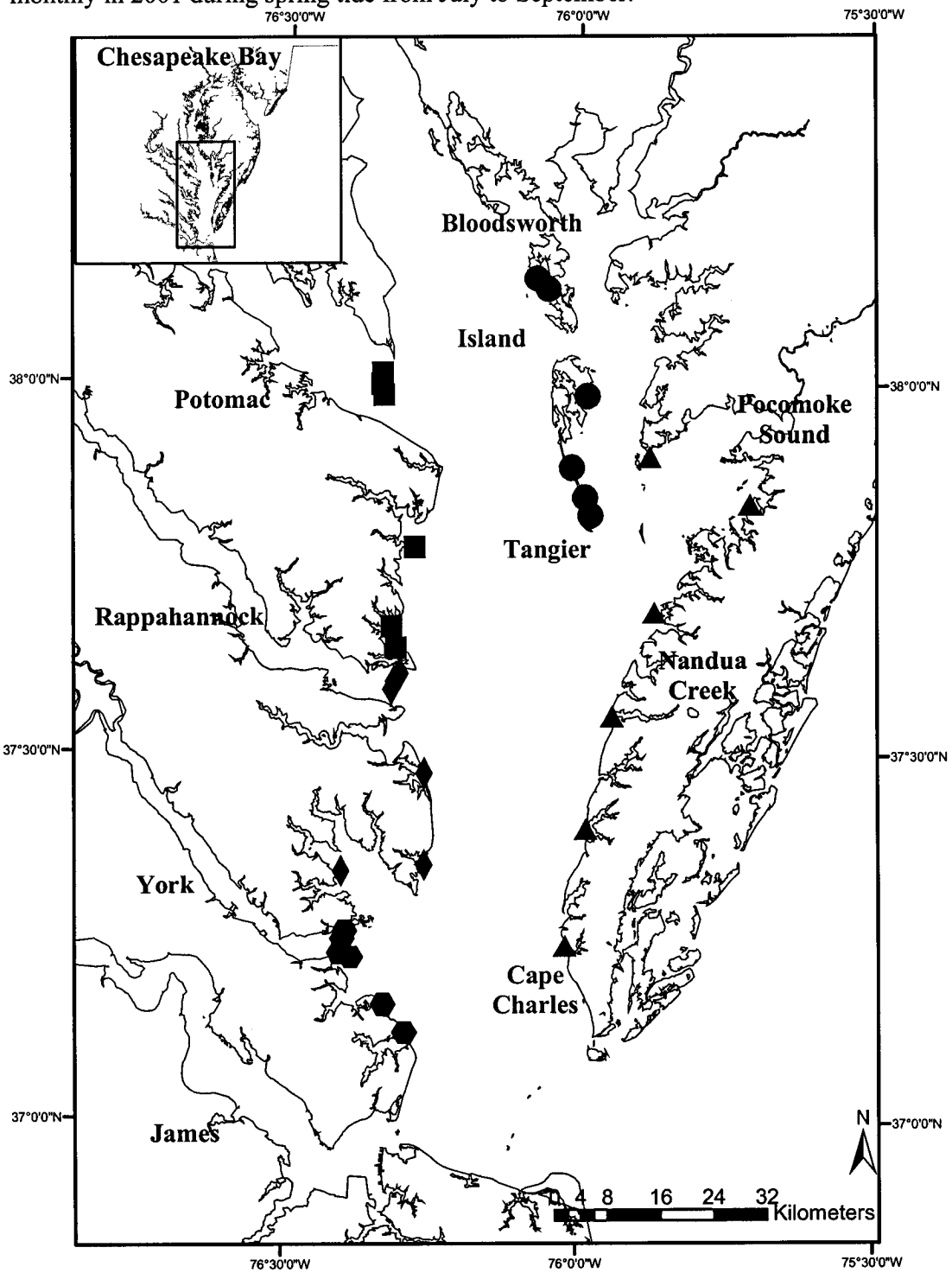
4.2.1. Sampling design

Juvenile spotted seatrout were collected in the five major seagrass habitats of the Chesapeake Bay: the Potomac, Rappahannock, York located in the Western Shore, the Islands in mid Bay, and the Pocomoke habitat located in the Eastern Shore from Pocomoke Sound to Nandua creek (Fig. 4.1). Using an otter trawl (0.64 cm stretched mesh, 7.9 m length), fish were randomly sampled at stations (seagrass beds) nested within habitats from July to September in 1998 and 2001. Juveniles were collected during spring tide once monthly in 1998, and twice monthly in 2001. Trawling was done using a 21-foot fiberglass boat, and for each station a minimum of three tows was made, which lasted two minutes each. Fish included in this study measured between 20 to 70 mm of standard length, which limited analysis to fish that had been exposed only to water chemistry of the seagrass habitats (Chapter III).

4.2.2. Analysis of otoliths

All sagittal otoliths were extracted from juvenile fish and prepared for analysis in a class-100 clean room. Right sagittal otoliths were prepared and analyzed using solution

Fig. 4.1. Map of the lower Chesapeake Bay showing the locations of sampling habitats and stations. Five seagrass habitats were sampled for juvenile spotted seatrout: Potomac, Rappahannock, York, Island, and Pocomoke. At each station, juvenile fish were randomly collected once monthly in 1998 and twice monthly in 2001 during spring tide from July to September.



based ICP-MS (see Chapter III). Quantification of trace elements was based on the method of external standard with internal standardization (Taylor 2001). I measured multiple trace elements in the otoliths but only four (Mn, Sr, Ba, and La) were selected due to their variability in surface waters of the Chesapeake Bay and their presence in otoliths (Chapter II and III). These trace elements were normalized to Ca to allow comparison with previous studies.

Oxygen and carbon isotopic composition of otoliths were quantified for fish collected in 2001. The left sagittae were ground and transformed into fine powder using acid-washed glass probes. From each sample 60 to100 μg of powder were collected and analyzed using a Micromass IsoPrime automated carbonate analyzer, based on the dual inlet measurement [by Dr. J. A. Kaufman at the Stable Isotope Laboratory (SIL), University of Maryland]. Samples were spiked with 102% phosphoric acid at a temperature of 90 °C. Ten otolith samples were sequentially analyzed after the measurement of five standard samples. The standards were prepared from limestone. Parameter acquisition was based on the coldfinger mode, leading to average precision of 0.004 and 0.006 (standard deviation) respectively for carbon and oxygen isotopic ratios. After analysis the raw data was corrected and reported in ‰ –PDB (Peedee belemnite) using the standard δ notation.

4.2.3. Statistical analyses

Statistical analyses of otolith trace elements and isotopes were performed using both parametric and non-parametric methods. I first used a 2 x 5 cross-factorial multivariate analysis of variance (MANOVA) to compare trace-element composition

among the five seagrass habitats and between 1998 and 2001. Secondly, for 2001only, I combined the stables isotope ratios, $\delta^{13}C$ and $\delta^{18}O$, with [Mn/Ca] and [Ba/Ca] and then used a one-way MANOVA to test for statistical significance of among-habitat difference. Because the presence of extreme outliers in the stable isotopes of juvenile fish from the Rappahannock resulted in too few samples, this habitat was excluded from the one-way MANOVA. The MANOVAs were performed after transforming the data as followed:

$$Y^{t}_{i,j} = Y_{i,j} * (S^{1/2}_{i,j})^{-1}$$

where $Y_{i,j}$ is the matrix of the four response variables in the i^{th} habitat and the j^{th} year, $S_{i,j}$ the estimate of variance-covariance matrix for the i^{th} habitat in the j^{th} year, and $Y^{t}_{i,j}$ the transformed matrix for the i^{th} habitat in the j^{th} year (Appendix II). This transformation ensures homogeneity of variance between the different treatment levels for each trace element. The assumption of homogeneity of within group-covariance matrices was met for residuals of both MANOVA models using Bartlett's maximum likelihood ratio test in SAS®[2]. Normality of residuals from the models was also tested for each element using the Shapiro-Wilk test. Some treatments departed from normality; therefore I used Pillai's Trace test, which is robust to departure from multivariate normality (Quinn and Queough 2002). Following the MANOVAs, I performed pairwise comparison of all habitats based on each variable using the Tukey Honestly Significant Difference (HSD) test. As the variance of the transformed data was similar among habitats, I used sample size within each habitat as weight during the performance of the HSD tests.

Further, I used a non-parametric method, the *k*-Nearest Neighbor discriminant analysis (*k-NN*) to determine the accuracy with which juvenile otolith microchemistry can be used to allocate individual fish to their natal habitat in each of the two years. This

method does not require normality or equality of the variance-covariance matrices between habitats (SAS 1988; Khattree and Naik 2000). Classification accuracy was based on the cross-validation method (Jacknife ~leave one out) in SAS®[2]. The best *k* value for each disriminant analysis was selected based on simulation.

To ensure that otolith weight did not confound statistical difference between years and among habitats, I examined the effect of otolith weight on otolith chemistry using both analysis of variance and regression analysis. Variations in otolith weight from juvenile spotted seatrout did not show significant interaction between year and habitat (ANOVA: df =4; MS= 4.01, p=0.145) and significant difference between habitats (ANOVA: df =4; MS= 1.33, p=0.68), but difference between years (ANOVA: df =1; MS= 58.21 p=0.0001) was highly significant. In addition, the trace elements were not significantly related to otolith weight in 2001, but they varied significantly with otolith weight in 1998. This clearly indicated that the slope of the regression of trace metals on otolith weight was different between the two years, and that a multivariate analysis of covariance could not be used. Therefore, I removed the effect of otolith weight on the trace elements of the 1998 collection by subtracting the slope of the regression multiplied by the otolith weight from the concentration of each element. The stable isotopes for 2001 samples were also adjusted due to significant variation in composition with otolith weight. Accordingly, all statistical analyses were performed on data where the effect of otolith weight was removed.

4.3. Results

4.3.1. *Trace element analysis*

Significant interaction between year and habitat was found for [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca] in otoliths of juvenile spotted seatrout (Table 4.1). Differences among habitats varied between years, and thus the concentration of trace elements in each habitat was not consistent over time and calls for separate comparison of habitats in each year. I present the results of the pairwise comparison test in Table 4.2.

Concentration of [Mn/Ca] measured in otoliths of Pocomoke habitat differed significantly from those of the Potomac, the York, and the Island in both years. In contrast, otoliths from the Pocomoke and the Rappahannock habitats had similar levels of [Mn/Ca] concentration in both years (Table 4.2). Although I have shown (Chapter III) that [Mn/Ca] in otoliths correlated positively with water chemistry, it was not evident that observed spatial differences would be preserved over time. [Mn/Ca] in otoliths from the Pocomoke habitat was significantly higher in both years compared to otoliths from the oceanic (York) and freshwater (Potomac and Island) end-member habitats, and these results indicate that the uptake of [Mn/Ca] in spotted seatrout otoliths may be conservative over time (Fig. 4.2). Campana (1999) suggested that [Mn/Ca] concentration in otoliths might not be physiologically regulated. Further, Mn concentration in Chesapeake Bay waters is controlled by redox reactions (Eaton 1979, Sholkovitz et al. 1992) rather than by salinity and mixing. Thus, independent of time, the effect of water chemistry on [Mn/Ca] in otoliths may result in an excellent biogeochemical tracer to identify fish that resided in the Pocomoke Sound as juveniles.

Levels of [Ba/Ca] measured in otoliths were relatively higher in 1998 than in

Table 4.1. Results of MANOVA of trace-element concentration and stable istotopic composition quantified in otoliths of juvenile spotted seatrout collected in seagrass habitats of the Chesapeake Bay.

a) MANOVA of [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca] measured in otoliths of fish collected in 1998 and in 2001 in five habitats: Potomac, York, Rappahannock, Island, and Pocomoke.

Source	Value	F	Numerator df	Denominator df	P
Year	0.749	11.96	4	143	0.0001
Habitat	1.727	27.73	16	584	0.0001
Year*Habitat	1.885	33.55	16	584	0.0001

b) MANOVA of [Mn/Ca], [Ba/Ca], [δ13C], [δ18O] measured in otoliths of fish collected in 2001 in four habitats: Potomac, York, Island, and Pocomoke.

Source	Value	F	Numerator df	Denominator df	P
Habitat	2.295	51.31	12	189	0.0001

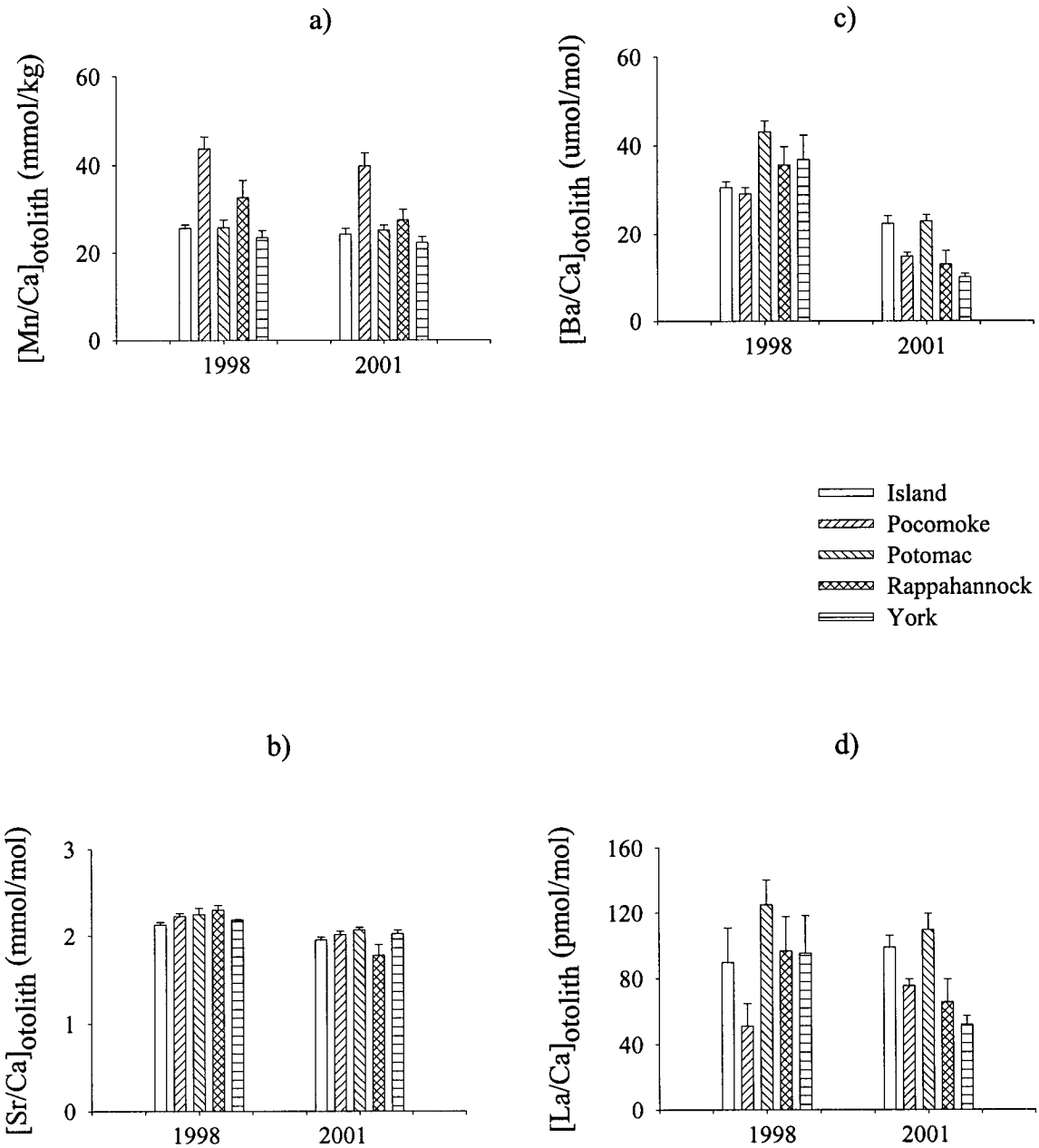
Note: All statistical analyses in tables 4.1a and 4.1b were based on transformed data and on Pillai's trace statistic.

Table 4.2. Results of weighted ANOVA for trace-element concentration and stables isotopic composition measured in otoliths of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay in 1998 and 2001.

	1998					2001				
Source	df	MS	F	P	HSD	df	MS	F	P	HSD
[Mn/Ca]										
Habitat	4	1525.98	70.34	0.0001	1,4	4	219.44	10.66	0.0001	1,5
Error	72	21.69			1,5	74	20.59			4,5
					2,4					3,5
					4,5					
					3,5					
[Sr/Ca]										
Habitat	4	2417.48	111.43	0.0001	1,all	4	317.40	15.41	0.0001	2,all
Error	72	21.69			2,all	74	20.59			
					5,all					
[Ba/Ca]										
Habitat	4	528.80	24.38	0.0001	1,2	4	485.92	23.59	0.0001	1,4
Error	72	21.69			1,5	74	20.59			1,5
					2,4					2,4
					3,5					4,5
					4,5					
[La/Ca]										
Habitat	4	439.89	20.28	0.0001	1,all	4	1371.89	66.61	0.0001	1,3
Error	72	21.69			4,5	74	20.59			1,4
										1,5
										2,3
										3,5
										3,4
[$\delta^{13}C$]										
Habitat						3	2029.87	101.64	0.0001	1,all
Error						67	19.97			4,all
[$\delta^{18}O$]										
Habitat						3			0.0001	1,all
Error						68				3,all

Note: Tukey Honestly Significant Difference (HSD) tests were based on transformed data. Habitats were labeled as:1= Potomac, 2 =Rappahannock, 3= York, 4= Island, 5= Pocomoke. The HSD columns show pair of habitats that were siginicantly different. "all" indicates that all other habitats were significantly different from the single habitat presented in a given HSD column.

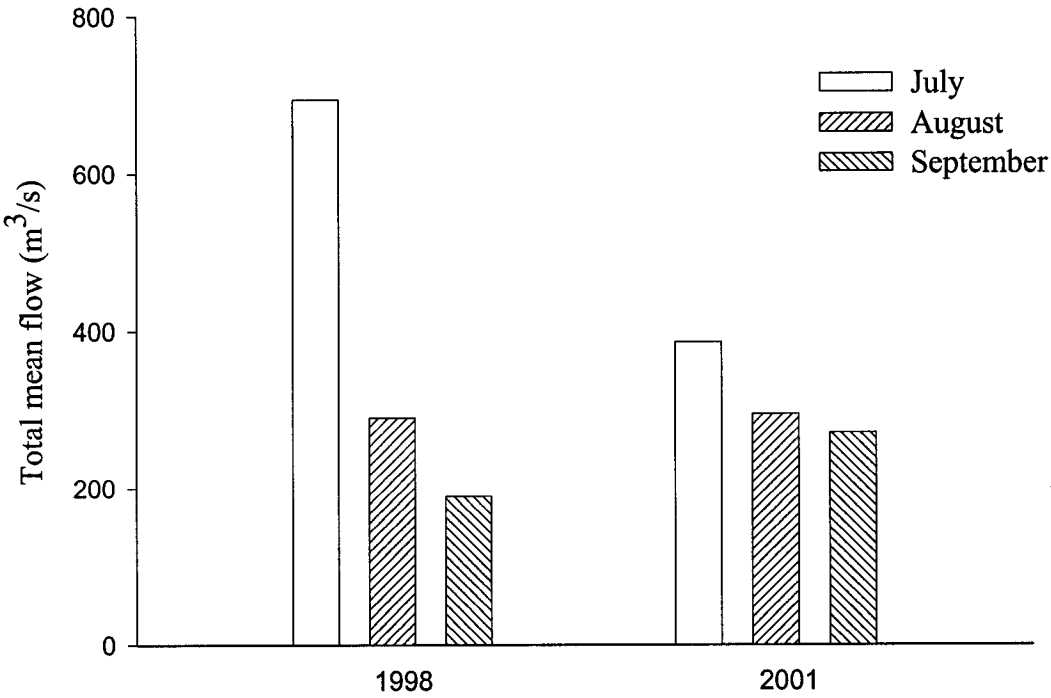
Fig. 4.2. Spatial and temporal variability in trace elements measured in otoliths of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay in 1998 and 2001. Data for the 1998 samples were adjusted for otolith weight.



2001, and statistical differences among habitats varied across years (Table 4.2). In 1998, [Ba/Ca] concentration in otoliths from the Pocomoke habitat was significantly different from the York, the Potomac, and the Island habitats, whereas in 2001 the Pocomoke habitat differed only from the latter two habitats. The Island had similar [Ba/Ca] levels as the Potomac in 1998, but in 2001 otoliths from those two habitats showed significantly different concentration (Table 4.2). Inter-annual variation of [Ba/Ca] in otoliths appeared to correlate with variability in freshwater input in the Bay, and consequently in the position of the salinity gradient relative to the fixed positions of the seagrass beds. Mean freshwater discharge in the Bay was, on average, higher in 1998 than in 2001 (Fig. 4.3). Because [Ba/Ca] in otoliths is negatively correlated with salinity (Chapter III) increased freshwater input in the Bay may have resulted in overall increase of Ba in juvenile otoliths. These changes in the flow regimes altered the spatial position of the salinity gradient, and likely the amount of trace elements observed in otoliths among the habitats in each of the two years.

Spatial variability of [La/Ca] in otoliths also fluctuated between years, but to a lesser extent than [Ba/Ca]. The concentration of [La/Ca] in otoliths of juvenile fish of the Potomac habitat was significantly different from the York, the Pocomoke, and the Island habitats in both years (Table 4.2). However, differences between the Potomac and the Rappahannock habitats varied between years. Similarly, [La/Ca] levels in otoliths of fish from the Island and the Pocomoke habitats were significantly different in 1998, but similar in 2001. Like [Ba/Ca], [La/Ca] measured in juvenile otoliths was best predicted by water salinity (Chapter III); therefore inter-annual variability in the magnitude of differences observed between habitats may be a result of change in the position of the

Fig. 4.3. Total mean monthly streamflow (m^3/s) from the Susquehanna and the Potomac Rivers measured by the USGS (station #015783310 & 01646500) in 1998 and 2001. Note that these two rivers account for 2/3 of the total freshwater input in Chesapeake Bay.



salinity gradient along and across the estuary.

Although there was significant difference among habitats in each year, [Sr/Ca] measured in otoliths varied little between years (Fig. 4.2). In both years otoliths from the Rappahannock habitat were significantly different from otoliths collected in all other habitats. The [Sr/Ca] concentration in otoliths from the Potomac was similar in 2001 to the Pocomoke, the Island, and the York habitats, but differed significantly from these three habitats in 1998. However, otolith concentration from fish sampled in the Island habitat was not significantly different from those of the York habitat in each of the two years (Table 4.2). This lack of differences across years of [Sr/Ca] concentration in otoliths indicated that this ratio did not reflect the distribution of salinity alone in the Bay in the two years.

4.3.2. Stable isotopes and trace elements in 2001

MANOVA results showed that otolith microchemistry between habitats was also significantly different, when [Mn/Ca] and]Ba/Ca] were combined with $\delta^{13}C$ and $\delta^{18}O$ for 2001 samples (Table 4.1a). Both stable isotopes contribute significantly to differences (Table 4.1b). Indeed, all habitats were significantly different between each other in $\delta^{13}C$, except the York and the Pocomoke habitats (Table 4.2). Further, $\delta^{18}O$ in the Island and Pocomoke habitats varied significantly from the Western Shore habitats. It is usually difficult to determine the cause of spatial differences in $\delta^{13}C$ of otoliths (Thorrold et al. 1998), because concentrations are due to both metabolic rate and water chemistry (Kalish 1991a, 1991b; Thorrold et al. 1997b). In contrast, $\delta^{18}O$ is highly correlated to temperature (Kalish 1991a, 1991b; Thorrold et al. 1997b) and $[Sr/Ca]_{water}$ (Chapter III).

Likewise, the differences in $\delta^{18}O$ may reflect different water sources, for example between the Potomac and the York (Table 4.2). Also, variability in $\delta^{18}O$ in otolith reflects spatial difference in water masses across the estuary. Although the Island and Pocomoke habitats were not significantly different in $\delta^{18}O$, there was a clear gradient across the Bay with $\delta^{18}O$ concentration being lower in the Pocomoke habitat, intermediate in the Island habitat, and higher in the Potomac habitat (Fig. 4.4).

4.3.4. Discriminant analysis

In 1998, when I classified individual fish based on their otolith microchemistry, the total classification error rate was 39% across all the five habitats (Table 4.3a) based on [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca]. Classification accuracy in the Potomac and the Island habitats were the highest (72-87 %), whereas samples from the Western Shore habitats were poorly classified (0-33%). Thus trace elements alone did not provide sufficient discrimination to classify individual habitat accurately.

In 2001, total error rate was lower (32%) compared to 1998 for the trace elements alone. Juvenile fish from the Pocomoke habitat showed high rate of classification (78%), compared to moderate rate in the Potomac, the York, and the Island habitats (63-70 %), and poor rate in the Rappahannock (20%) (Table 4.3b). These results indicate that irrespective of the year, trace elements in otoliths may be used to distinguish the juvenile fish that sojourn in the Pocomoke from those fish residing in any other seagrass habitats. However, the ability of trace elements alone to identify juvenile fish born in the Island habitat from those born in the Western Shore habitats may vary between years. Further, the trace elements showed little ability to separate the York and the Rappahannock from

Fig. 4.4. Spatial variability in [$\delta^{13}C$] and [$\delta^{18}O$] measured in otoliths of juvenile spotted seatrout collected in seagrass habitats of Chesapeake Bay in 2001. All data were adjusted for otolith weight.

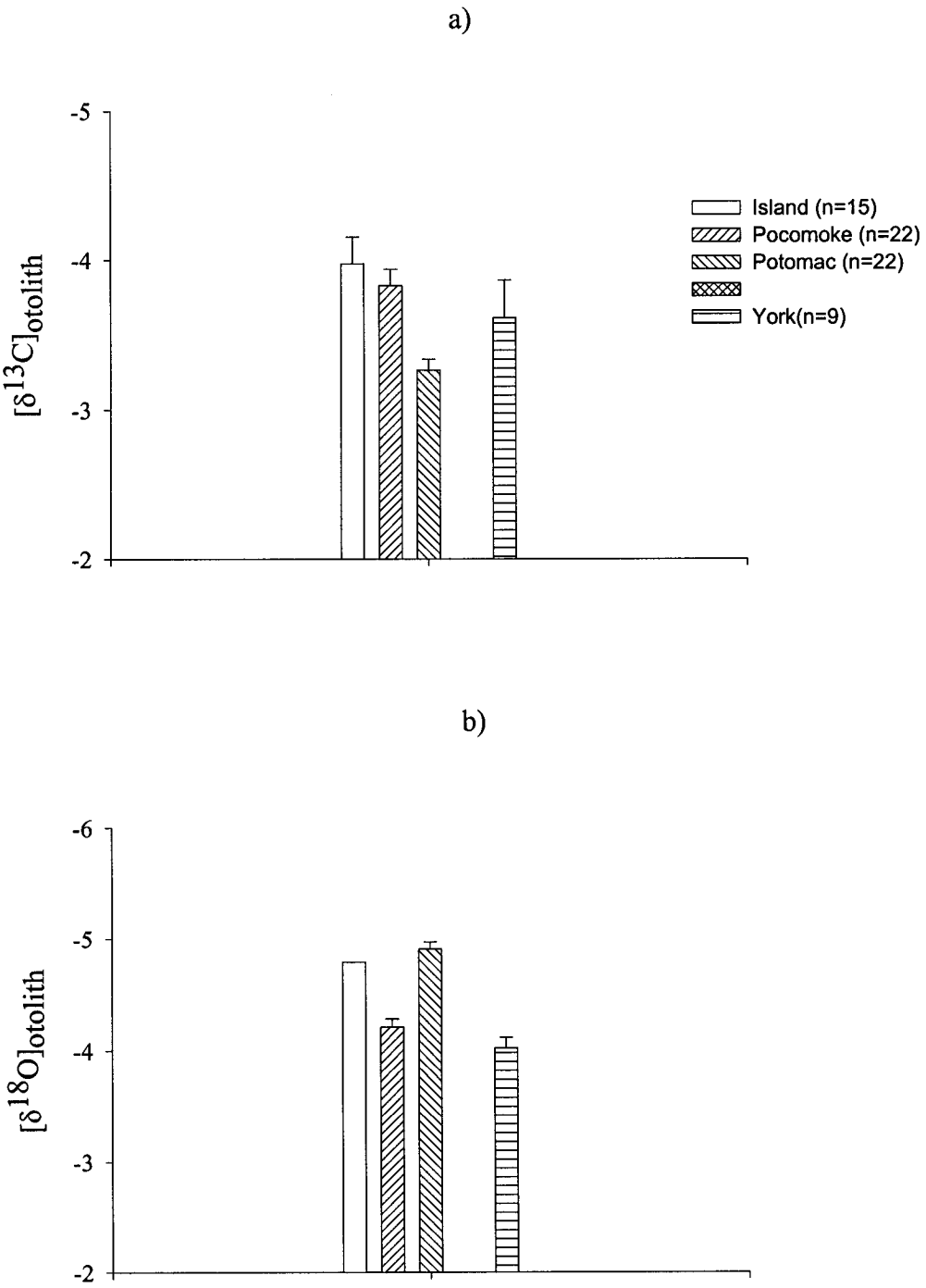


Table 4.3. Results of *k*-nearest neighbor discriminant function analysis for classifying individual juvenile spotted seatrout to five seagrass habitats based on trace element concentration and stable isotopic composition.

a) [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca] measured in 1998 otoliths ($k = 4$)

Sample source	Potomac	Rappahannock	York	Island	Pocomoke	Other
	Cross-validation accuracy (%)					
Potomac (n=9)	**33.3**	0.0	11.1	22.2	22.2	11.2
Rappahannock (n=8)	0.0	**12.5**	12.5	25.0	37.5	12.5
York (n=7)	42.9	0.0	**0.0**	42.9	14.3	0.0
Island (n=22)	9.1	0.0	0.0	**73.7**	13.6	4.6
Pocomoke (n=31)	3.2	3.2	0.0	6.5	**87.1**	0.0

b) [Mn/Ca], [Sr/Ca], [Ba/Ca], and [La/Ca] measured in 2001 otoliths ($k = 4$)

Sample source	Potomac	Rappahannock	York	Island	Pocomoke	Other
	Cross-validation accuracy (%)					
Potomac (n=22)	**70.4**	0.0	0.0	22.2	3.7	3.7
Rappahannock(n=5)	20.0	**20.0**	0.0	20.0	20.0	20.0
York (n=9)	0.0	0.0	**62.5**	0.0	25.0	12.5
Island (n=15)	31.3	0.0	0.0	**62.5**	0.0	6.3
Pocomoke (n=22)	8.7	0.0	13.0	0.0	**78.3**	0.0

c) [Mn/Ca], [Ba/Ca], [$\delta^{13}C$], [$\delta^{18}O$] measured in 2001 otoliths ($k = 2$)

Sample source	Potomac	York	Island	Pocomoke	Other
	Cross-validation accuracy (%)				
Potomac (n=22)	**95.5**	0.0	0.0	4.5	0.0
York (n=9)	0.0	**100.0**	0.0	0.0	0.0
Island (n=15)	20.0	0.0	**80.0**	0.0	0.0
Pocomoke (n=22)	0.0	9.1	0.0	**81.8**	9.1

Note: Trace-element concentration in 1998 and stable isotopic composition in 2001 were adjusted for otolith weight. Other = category of otoliths that could not be classified to either habitat after Jacknife Cross-Validation.

other habitats. This could be expected for the Rappahannock habitat, because trace elements in surface waters of this habitat also did not separate from the other habitats (Chapter II).

However, when [Mn/Ca], [Ba/Ca] were combined with $\delta^{13}C$ and $\delta^{18}O$ in 2001, error rates improved significantly totaling 12% across the Potomac, the York, the Pocomoke, and the Island habitats (Table 4.3c). The combination of elemental and isotopic composition of juvenile otoliths resulted in clear separation of the two Western Shore habitats from the Islands and the Pocomoke Sound. Thorrold et al. (1998) previously observed similar enhancement in classification rate when stable isotopes were combined with trace elements to distinguish natal estuaries for juvenile weakfish. Although I used a different discriminant functions than Thorrold et al. (1998), my results suggested that at a smaller spatial scale, within an estuary, stable isotopes would be as useful in discriminating natal habitats based on otolith microchemistry.

4.4. Discussion

Chemical composition of otoliths of juvenile spotted seatrout caught in seagrass habitats in the lower Chesapeake Bay show significant variability within and between years. The ability of trace elements to record natal habitat of individuals in the estuary varies between years, and the use of oxygen and carbon stable isotopes may be necessary in some years to increase correct classification. In this context, my study demonstrates that small-scale spatial variation in otolith microchemistry may be used in the Bay to identify specific seagrass beds with the promise that they can be used as natural tags to measure subsequent survival and to determine essential seagrass habitats.

Small-scale spatial differences in the elemental composition of juvenile spotted seatrout otoliths are consistent with previous observations by Gillanders and Kingsford (2000) and Gillanders (2002). These authors observed that otoliths of juvenile *Pagrus auratus* and *Pelates sexlineatus* could record spatial heterogeneity in estuarine habitats in the scale of hundreds of meters to a few kilometers. Despite small sample size (5-7 per site), variability in Mn, Sr, and Ba allowed Gillanders and Kingsford (2000) to classify juvenile *Pelates sexlineatus* to their site of recruitment with high accuracy averaging 75% in each of two consecutive years. However, both Gillanders and Kingsford (2000) and Gillanders (2002) did not record information on water chemistry at the different sites of collection. Therefore these authors could only speculate on the effects of water chemistry on the variability of otolith microchemistry between sites. In contrast, for 2001 my study explores small-scale spatial variation in otolith microchemistry based on known trace- element concentration in surface waters of the Chesapeake Bay. Therefore, I could directly assess the variability of otolith microchemistry between habitats relative to the change in water chemistry for each element. In Chapter (III) I demonstrated that salinity explained most of the variation in [Ba/Ca] and [La/Ca] concentration in otoliths. Contrary to expectation, variation of [Sr/Ca] in otoliths was not explained by salinity or [Sr/Ca] in water. Further, small-scale variation in [Mn/Ca] concentrations in otoliths was also independent of salinity and resulted mostly from reducing process in surface sediment and bottom waters of the Bay. While [Mn/Ca] in surface waters of the Chesapeake Bay is controlled by redox reactions (e.g., Eaton 1979; Gavis and Grant 1986 Sholkovitz et 1992), in other estuaries [Mn/Ca] concentration is regulated by mixing (e.g., Sholkovitz 1978, Paucot and Wollast 1997), potentially leading to different

interaction with otolith microchemistry. These behaviors of otolith trace elements emphasize the value of prior knowledge of water chemistry before the causes of spatial variation can be fully understood.

Results from this study are also important because previous authors (e.g., Kimura et al. 2000, Secor et al. 2001) mostly relied on indirect evidence to study fish population dynamics and their life history strategies in estuaries. Kimura et al. 2000 used [Sr/Ca] to reconstruct past up-estuary dispersal of young-of-the year (YOY) bay anchovy, *Anchoa mitchilli*, along a steep gradient of salinity (0 – 29 ppt) from the head to the mouth of the Chesapeake Bay. These authors predicted salinity from [Sr/Ca] measured in YOY otoliths using electron microprobe analysis (EPMA). However, as the author admitted, there were no direct experimental evidences that otoliths of bay anchovy could accurately predict water salinity. In addition, bay anchovy is a vagile species that occurs in both shallow and deep water of estuaries, exhibiting diurnal migration in the water column (Rilling and Houde 1999, Schultz et al. 2003). Because there are significant lateral and vertical differences in the density field of the Chesapeake Bay (Valle-Levinson and Atkinson 1999, Chapter II), locating natal habitat for such mobile species is likely to be associated with high uncertainties.

Similarly, Secor et al. (2001) retrospectively discriminated groups of striped bass, *Morone saxalis*, inhabiting estuarine habitats in the Hudson River from those using coastal habitats. Their study examined habitats that encompass the whole salinity gradient from fresh to oceanic waters in a one-river dominated estuary. In such system there may be little lateral variability in the density field and in trace elements (Smith 1977), and differences observed in otolith microchemistry may be solely driven by the

steep gradient in salinity between freshwater and oceanic end-member habitats. However, my study in Chesapeake Bay shows that even outside the steep salinity gradient fine spatial differences in otolith microchemistry can be determined. In contrast to the Hudson River, there is lateral variability in the trace-element microchemistry of surface waters of the Chesapeake Bay, and such lateral heterogeneity is regulated not only by salinity, but also by competing and redox reactions (see Chapter II).

For 2001, my study is the first to directly link the effect of inter-annual variability in otolith microchemistry to environmental changes in estuaries. My data suggested that mixing of fluvial and oceanic waters would determine the extent of annual fluctuation in [Ba/Ca] and [La/Ca] measured in otoliths, whereas reducing processes in surface sediment and bottom waters in Chesapeake Bay will regulate [Mn/Ca]. In contrast to [Mn/Ca], [Ba/Ca], and [La/Ca], physiology may interact with other factors to influence inter-annual variation in [Sr/Ca]. Therefore though both salinity and [Sr/Ca] concentration in water varies annually with freshwater discharge in the Bay, these variations are not unambiguously recorded in otoliths. This is counter to Kimura et al. (2000) and Secor et al. (1995), which hypothesized that otolith [Sr/Ca] in bay anchovy and striped bass can predict water salinity, and thus locate natal habitats. Nevertheless, my results support the argument of previous authors (i.e., Milton et al. 1997; Gillanders 2002) that temporal and spatial heterogeneity can be confounded, leading to biased predictions if data from a single year are used to classify fish to natal estuaries for different cohorts.

While some authors have determined that trace elements can be useful to discriminate populations within and between estuaries, few studies have used them in

combination with stable isotopes (Thorrold et al. 1998, Thorrold et al. 2001). Thorrold et al. (1998, 2001) found that the ability to discriminate between juvenile fish born in different estuaries of the U.S East Coast, and to retrospectively classify adult fish to their natal habitats was increased when $\delta^{13}C$ and $\delta^{18}O$ were added to [Mg/Ca], [Mn/Ca], [Sr/Ca], and [Ba/Ca]. However, Thorrold et al. (1998) were uncertain whether the enhanced accuracy of the carbon and oxygen isotopic composition would come at the expense of higher error rates due to inter-annual variations within the different estuarine systems. In that respect, my study suggests that at small-scale, within estuary, inter-annual variability in the flow regime will alter the accuracy with which trace elements in otoliths can allocate fish to their natal habitat, and thus the use of stable isotopes may be necessary to improve accuracy in most years. The stable isotopic composition of otoliths provides independent information that is not recorded by Mn, Sr, and Ba as shown for spotted seatrout. Inclusion of $\delta^{18}O$, for example, improved discrimination between habitats located at the oceanic and freshwater end-members in the lower Bay, and recorded lateral differences in the density field.

The discrimination of seagrass habitats in the lower Chesapeake Bay based on otolith microchemistry has important conservation implications. First, the distinct chemical signatures of juveniles inhabiting different seagrass habitats is evidence that the core of otoliths from spawners could be analyzed to retrospectively determine which habitats contribute most to the adult populations of spotted seatrout. Because the Chesapeake Bay spotted seatrout are genetically separated from other populations along the U.S Atlantic East Coast (Wiley and Chapman 2003), these fish are reproductively isolated. Therefore, the estimation of seagrass-specific survivorship can be done

accurately, because there is low probability that recruitment from other estuaries would be a confounding factor. Further, straying and introgression can be assessed based on techniques already shown to be effective in weakfish (Thorrold et al. 2001). However, due to inter-annual variability survivorship should be estimated on a cohort-specific basis and multiple cohorts may need study before the most essential habitats can be identified, if such exist consistently over time.

If the most essential habitats can be identified for juvenile spotted seatrout as I propose, conservation strategy can become more efficient by targeting the habitats that produce the fittest individuals. Based on its life-history characteristics spotted has been hypothesized to be an indicator of estuarine conditions (Bortone 2003). Therefore, restoring the most essential habitats for juvenile spotted seatrout may ensure the maintenance of the population, while providing a biological means to monitor the health of the Chesapeake Bay and its living community.

4.5. Conclusion

Otolith microchemistry of juvenile spotted seatrout caught in seagrass habitats in the lower Chesapeake showed significant variability within and between years. Although the ability of trace elements to allocate individual fish to their nursery habitats may vary between years, in combination with oxygen and carbon stable isotopes they provide a robust method to achieve high classification accuracy. In that respect, my study demonstrated clearly that otolith microchemistry might be used in the Chesapeake Bay to identify essential seagrass habitats for juvenile spotted seatrout. However, due to inter-

annual variability a monitoring program would be required to study multiple cohorts before the most important habitats can be identified, if such exist consistently over time.

CHAPTER V

SUMMARY

A quantitative understanding of habitat use of estuarine-dependent fish populations is critical to the conservation of their most essential habitats. Because recruitment and fitness may be influenced by the quality of larval and juvenile habitats, developing habitat-specific methods to quantify the vital rates and elucidating life history dynamics of these life stages are pivotal to such understanding. I investigated the spatial and temporal variability in the chemistry of surface waters and otoliths of juvenile spotted seatrout collected in five seagrass habitats of the lower Chesapeake Bay: Potomac, Rappahannock, York, Island, and Eastern Shore. I measured Mg, Ca, Mn, Sr, Ba, and La by inductively-coupled plasma mass spectrometry, and $\delta^{13}C$ and $\delta^{18}O$ using an automated carbonate analyzer. Despite temporal variability, there was significant spatial variability in surface water chemistry and otolith microchemistry of seagrass habitats in the Bay. I found clear evidence that biogeochemical signatures in otoliths could be used to estimate habitat-specific survivorship for spotted seatrout, and therefore may be useful in identifying the most essential seagrass habitats for their juveniles in the Bay.

Longitudinal and lateral variability in the minor- and trace-element chemistry of surface waters was consistent with anticipated patterns from the physical characteristics of the Chesapeake Bay. However, this study provides the first field test that shows significant lateral difference in surface water chemistry of the Bay in the scale of 10 to 50 km. Despite temporal variability, the chemistry of surface waters in the five seagrass habitats was significantly distinct. This was attributed not only to the influence of

salinity, but also to competing reactions between elements such as Ba and Mg, and redox control of Mn. The chemistry of the Island habitat was unique, potentially because of the influence of Coriolis acceleration and resulting chemistry from freshwater and sediment loads of the Susquehanna River. These results strongly suggest there was restricted flow between habitats, and those organisms that live in these habitats for prolonged periods of time experienced different water mass exposures.

This study provides the first field-based experiment that directly relates otolith microchemistry to water chemistry in an estuary. I found that there were predictive relations for elements that are not physiologically controlled and that are not sensitive to temperature, such as [Ba/Ca] and [La/Ca]. Salinity could predict accurately $[Ba/Ca]_{otolith}$, and $[La/Ca]_{otolith}$, and there was positive correlation between $[Ba/Ca]_{otolith}$ and $[Ba/Ca]_{water}$. However, the relation between $[Ba/Ca]_{otolith}$ and $[Ba/Ca]_{water}$ was not linear as predicted in laboratory-controlled experiments. Contrary to expectation, $[Sr/Ca]_{otolith}$ did not correlate with water chemistry directly. These results emphasize that variability in the trace-element chemistry of otoliths may be species-specific, and that findings from laboratory experiments would need validation before being applied. In addition, given the magnitude of lateral variability in both waters and otoliths, I determined that water chemistry could not be used as surrogate for otolith microchemistry in wide estuaries. Therefore, a library of juvenile otoliths would be required to study life history and dynamics of fishes in such systems.

This study establishes a scientific framework to start linking survivorship of juvenile spotted seatrout from their summer residence in natal seagrass habitats to their return in the Bay to spawn in the subsequent late spring. Chemical composition of

otoliths of juvenile spotted seatrout collected in the five seagrass habitats showed significant variability within and between years. The ratio of [Mn/Ca] in otoliths was the only element whose spatial variation was conservative over time. Due to inter-annual variability in the physical and chemical processes in the Bay, the ability of trace-element signatures to allocate individual fish to their nursery habitats may vary between years (0% to 82%). However, the combination of trace elements with oxygen and carbon stable isotopes may constitute a robust method to achieve high classification accuracy. Indeed, classification accuracy of juvenile fish to their natal habitats, based on [Mn/Ca], [Ba/Ca], $\delta^{13}C$, and $\delta^{18}O$ in otoliths varies from 82 to 100% for fish collected in 2001. These results demonstrate clearly that otolith microchemistry can be used in the Chesapeake Bay to identify essential seagrass habitats for juvenile spotted seatrout. However, due to inter-annual variability, a monitoring program would be required to study multiple cohorts before the most important habitats can be identified, if such exist consistently over time.

In conclusion, spatial variations in the chemistry of surface waters and otoliths are fully resolvable across all seagrass habitats in the lower Chesapeake Bay. Knowledge of the otolith microchemistry of these habitats can allow the estimation of habitat-specific survivorship for spotted seatrout. Differential survivorship may be used as proxy for fitness to identify habitats that contribute most recruits to the maintenance of the Chesapeake Bay population. This has important management implications, because these habitats would be the most essential to preserve for the sustainable exploitation and conservation of spotted seatrout.

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APPENDIX I

PROCEDURE FOR PERFORMING WEIGHTED REGRESSION

1) Test for lack of linear fit

a) Compute SS -Pure error (SS_{PE})

$$SS_{PE} = (n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + (n_3 - 1)s_3^2 + (n_4 - 1)s_4^2 + (n_5 - 1)s_5^2$$

with s_i^2 being the variance of $[Me/Ca]_{otolith}$ the i^{th} habitat, and n the sample size (number of otolith samples) in the i^{th} habitat.

b) Compute SS-Lack of fit (SS_{LE})

$SS_{LE} = SSE - SS_{PE}$

SSE is obtained by fitting regression to all the data (meaning all otoliths samples), with the mean of salinity or $[Me/Ca]_{water}$ as independent fixed factor.

c) Compute the F test based on

$$F = MS_{LE} / MS_{PE}$$

2) Perform correct regression analysis using weighted regression based on:

$\bar{y}_i$ being the mean of $[Me/Ca]_{otolith}$ in the i^{th} habitat

$w_i = \frac{n_i}{s_i^2}$ being the weight for the i^{th} habitat (with *i varying* from 1 to 5),

and the mean of salinity or mean $[Me/Ca]_{water}$ as independent fixed factor.

APPENDIX II

PROCEDURE FOR TRANSFORMING DATA IN EACH HABITAT AND IN EACH YEAR

For each habitat I compute the maximum likelihood estimate of the variance-covariance

$$S_n = (\frac{1}{n})Y'(I_n - (\frac{1}{n})1_n 1_n')Y$$

With n in the sample size in a given habitat

I the identity matrix

1_n the n by vector of unit elements

Y is the matrix of the original data

Y' is the transpose of Y

S_n is the sample dispersion matrix (with df as denominator)

Then I compute the square root of S_n:

$$S_n^{1/2}$$

Thereafter, the matrix was transformed as:

$$Y^t = Y * (S_n^{1/2})^{-1}$$

N.B.: To perform all transformations I modified a SAS program provided by Dr. Dayannand N. Naik.

APPENDIX III- 2001 WATER CHEMISTRY DATA

Coll. date	Habitat	Station	DO mg/L	pH	Salinity per mil	Mg (mmol/kg)	Mn nmol/kg	Sr umol/kg	Ba nmol/kg
7/10	4	4	7.35	8.40	15.60	26.16	22.40	65.94	170.46
7/10	4	5	7.88	8.47	17.40	31.04	7.93	46.43	330.67
7/10	4	29	7.95	8.54	17.50	31.01	11.65	47.73	332.24
7/10	4	30	8.14	8.47	17.00	29.35	20.14	49.59	334.48
7/10	4	33	7.50	8.42	15.40	26.04	14.46	39.54	356.39
7/11	5	25	7.49	8.34	19.30	33.29	21.97	50.58	249.53
7/11	5	27	10.50	8.63	17.70	31.24	56.60	46.77	346.66
7/11	5	28	7.20	8.04	19.70	34.25	67.69	50.30	370.86
7/12	5	22	7.43	8.37	22.40	39.25	12.70	61.31	211.20
7/12	5	23	7.13	8.28	24.40	45.86	13.65	61.61	235.77
7/12	5	24	7.16	8.40		32.65	8.20	52.28	235.32
7/13	1	9	7.35	8.41	16.30	28.33	4.96	44.74	318.66
7/13	1	10	7.56	8.48	17.50	30.73	4.41	48.56	303.78
7/13	1	11	7.76	8.52	17.40	31.06	3.58	46.33	287.10
7/13	1	2*	6.70	8.33	13.90	23.84	1.76	35.82	370.68
7/13	2	12	8.10	8.44	17.70	24.85	8.90	46.17	309.14
7/13	2	13	10.45	8.64	19.90	34.11	12.91	53.84	262.67
7/13	2	16	7.14	8.23	20.10	34.14	42.55	58.64	283.94
7/13	2	2*	7.61	8.36	16.70	28.31	2.25	44.12	317.66
7/16	3	17	6.24	8.34	21.70	37.09	2.43	63.53	260.44
7/16	3	18	6.30	8.14	21.70	40.68		57.36	257.51
7/16	3	19	5.62	8.12	21.40	38.64	45.66	40.95	362.71
7/16	3	2*	6.39	8.24	21.03	35.89	19.02	55.95	244.90
7/23	5	23	8.16	9.16	26.50	44.30	18.16	82.17	163.57
7/23	5	24	8.18	7.93	21.30	37.00	11.57	54.90	217.57
7/23	5	25	8.20	7.80	19.40	34.04	16.69	58.76	358.43
7/23	5	27	7.82	6.38	18.70	31.07	341.93	53.25	424.73
7/23	5	28	8.03	7.08	19.10	33.43	30.57	56.67	418.64
7/25	2	12	9.54	8.47	18.90	32.17	20.35	58.99	347.99
7/25	2	13	7.08	8.01	18.70	33.47	11.99	55.86	333.12
7/25	2	16	7.37	8.13	20.30	35.24	24.31	57.16	297.96
7/25	2	2*	7.82	8.24	17.27	30.09	4.09	51.76	348.15
7/25	3	17	5.83	7.77	21.50	37.50	39.04	60.23	273.86
7/25	3	18	4.10	7.45	22.50	37.26	172.75	71.01	343.66
7/25	3	19	6.21	7.83	21.50	38.31	49.24	63.43	278.82
7/25	3	2*	6.01	7.87	21.90	39.21	14.22	60.87	263.33
7/26	1	9	7.25	8.27	17.00	30.07	4.53	47.14	336.75
7/26	1	10	6.65	8.19	18.30	31.93	10.31	50.12	310.06
7/26	1	11	6.32	8.03	20.60	32.21	5.61	58.70	287.01
7/26	1	2*	7.64	8.30	14.83	26.10	1.34	43.27	406.19
7/27	4	4	8.25	8.22	16.00	27.83	6.71	51.14	480.48
7/27	4	5	7.15	8.06	18.30	32.71	5.45	47.31	287.34
7/27	4	29	6.98	7.99	17.40	29.47	7.76	52.04	357.84
7/27	4	30	7.40	8.06	17.70	31.64	6.51	49.35	387.04
7/27	4	31	7.53	8.02	17.70	30.17	23.63	53.49	409.54
7/27	4	33	8.90	8.32	16.10	27.53	14.39	45.74	402.52
8/6	2	12	6.82	8.09	19.30	29.39	28.57	60.16	375.06

APPENDIX III "Continued"

Coll. date	Habitat	Station	DO mg/L	pH	Salinity per mil	Mg (mmol/kg)	Mn nmol/kg	Sr umol/kg	Ba nmol/kg
8/6	2	13	8.06	8.19	21.60	35.18	16.66	64.92	302.46
8/6	2	16	7.33	8.14	21.00	24.51	4.11	71.42	319.29
8/6	3	17	5.76	8.19	22.80	36.86	56.70	61.19	254.68
8/6	3	18	5.35	7.80	23.20			85.60	308.13
8/6	3	19	6.52	8.02	22.60	39.26	13.35	72.84	272.05
8/6	3	2*	6.40	8.01	22.27	39.22	14.23	74.95	284.47
8/7	1	9	7.35	8.07	17.50	28.39	11.83	60.30	407.96
8/7	1	10	6.70	8.08	18.20	32.34	8.85	57.76	380.39
8/7	1	11	6.65	8.00	18.80	32.42	5.19	63.48	346.92
8/7	1	2*	7.66	8.18	14.97	25.80	4.31	47.38	427.35
8/7	2	2*	7.32	8.13	17.43	31.06	1.68	62.05	394.76
8/8	5	22	6.85	8.02	22.40			72.67	272.15
8/8	5	23	6.50	7.91	24.80	43.91	16.57	87.27	226.77
8/8	5	24	9.75	8.33	20.40	34.66	18.21	64.32	309.46
8/8	5	25	6.36	7.82	19.80	35.56	16.84	61.63	329.50
8/8	5	27	6.78	8.05	18.80	27.40	44.13	62.68	424.35
8/8	5	28	8.84	8.05	19.50	32.62	69.83	61.26	410.09
8/9	4	4	6.94	8.06	16.50	25.94	13.03	60.10	490.52
8/9	4	5	6.83	8.06	18.60	32.57	16.04	54.61	370.40
8/9	4	29	6.70	8.01	18.60		0.00	59.61	380.14
8/9	4	30	7.50	8.08	18.30	33.86	13.67	57.95	405.90
8/9	4	31	6.80	8.02	18.50	32.66	17.87	65.36	431.99
8/9	4	33	7.35	8.10	16.40	27.87	8.06	54.34	456.36
8/20	4	4	7.13	8.16	16.10	27.69	7.29	48.06	432.76
8/20	4	5	7.20	8.05	17.20	27.44	10.29	55.23	363.08
8/20	4	29	6.29	8.07	18.00	26.88	4.56	54.27	344.08
8/20	4	30	9.96	8.25	17.30	24.76	29.24	51.28	354.58
8/20	4	31	6.96	7.99	17.50	30.40	16.98	55.63	387.64
8/20	4	33	7.24	8.16	16.10	29.69	6.95	48.51	420.07
8/21	5	22	8.92	8.23	21.80	38.98	22.42	68.93	247.55
8/21	5	23		8.23	23.20	33.98	5.12	70.71	236.86
8/21	5	24				30.66	7.21	58.29	274.18
8/21	5	25	6.06	7.88	19.60	27.08	52.44	58.79	315.27
8/21	5	27	5.14	7.93	18.40	28.18	32.79	59.08	364.57
8/21	5	28	4.69	7.53	18.00	30.00	56.89	55.28	355.96
8/22	1	9	6.79	8.29	16.70	25.90	3.46	46.93	332.86
8/22	1	10	6.46	8.22	18.10	32.92	7.29	55.33	356.56
8/22	1	11	6.95	8.24	18.20	32.05	6.47	55.76	318.29
8/22	2	12	7.81	8.25	18.60	32.92	19.93	56.47	327.92
8/22	2	13	8.14	8.29	21.40	32.73	7.44	64.40	269.90
8/22	2	16	8.30	8.26	20.40	27.48	36.88	64.11	289.48
8/23	3	17	9.10	8.35	22.30	39.03	32.24	61.66	260.81
8/23	3	18	7.70	8.20	22.50	39.90	7.07	64.78	242.48
8/23	3	19	8.15	8.19	22.10	14.37	0.98	67.25	271.59
9/4	4	4	7.02	8.05	15.80	31.20	4.51	52.25	487.91
9/4	4	5	7.59	8.00	18.70	32.23	13.35	63.09	383.40
9/4	4	29	7.16	8.08	18.70	32.17	4.49	59.29	385.43

APPENDIX-III "Continued"

Coll. date	Habitat	Station	DO mg/L	pH	Salinity per mil	Mg (mmol/kg)	Mn nmol/kg	Sr umol/kg	Ba nmol/kg
9/4	4	30	8.72	8.11	18.00	31.61	31.64	54.96	428.18
9/4	4	31	7.67	7.96	18.10	24.32	12.84	54.91	455.47
9/4	4	33	7.26	8.07	16.10	25.91	8.38	51.24	450.36
9/5	5	22	9.57	8.27	23.80	35.06	12.03	74.34	267.55
9/5	5	24	7.80	8.13	21.10	33.91	6.24	65.60	305.50
9/5	5	25	6.79	7.97	20.40	31.73	12.02	66.06	322.41
9/5	5	27	5.77	7.67	18.70	27.89	45.76	59.63	401.16
9/5	5	28	6.92	7.91	18.70	32.05	22.51	56.96	419.45
9/7	1	9	6.36	8.14	17.60	30.07	3.34	55.28	359.74
9/7	1	10	6.72	8.10	18.51	29.99	2.90	59.77	371.78
9/7	1	11	6.50	8.10	19.00	33.11	3.51	59.93	348.90
9/7	2	12	8.66	8.19	18.50	31.73	18.87	62.57	343.69
9/7	2	13	7.86	8.13	20.70	34.87	13.32	65.81	323.18
9/7	2	16	8.13	8.10	21.60	35.32	20.36	72.87	303.19
9/7	3	17	7.90	8.00	22.00	36.53	12.42	69.00	292.60
9/7	3	18	7.36	7.95	22.30	31.01	10.46	72.70	289.78
9/7	3	19	8.86	8.12	22.60	34.51	15.09	69.85	283.96
9/17	4	5	9.03	8.11	18.40	30.32	3.74	55.16	397.23
9/17	4	29	7.72	7.91	17.80	31.90	4.11	61.86	383.47
9/17	4	30	9.42	8.14	18.80	32.64	6.51	59.28	381.57
9/17	4	31	9.60	7.98	18.10	26.42	17.60	55.28	425.18
9/17	4	33	8.36	8.04	17.20	31.09	7.27	55.52	409.86
9/18	1	9	7.27	8.06	18.10	30.24	6.78	54.11	349.85
9/18	1	10	7.73	8.06	18.50	31.00	3.28	57.36	325.55
9/18	5	22	8.87	8.04	24.70	38.29	20.47	77.94	241.44
9/18	5	23	8.83	8.04	25.70	37.27	14.83	79.95	234.33
9/18	5	24	8.59	8.09	21.10	31.55	15.51	65.16	327.80
9/18	5	25	8.02	7.98	20.30	33.24	20.12	60.92	346.53
9/18	5	27	6.78	7.92	19.40	31.19	17.91	60.34	382.00
9/18	5	28	6.98	7.82	19.10	30.12	34.35	59.61	400.53
9/19	1	11	7.97	8.07	18.60	31.10	4.07	59.19	359.91
9/19	2	12	7.80	8.07	18.90	34.47	76.62	57.43	354.08
9/19	2	13	8.17	8.10	21.20	35.01	11.31	63.91	308.44
9/19	3	17	5.30	7.57	23.50	37.52	52.54	74.61	293.69
9/19	3	18	6.56	7.89	22.90	35.23	12.36	70.13	275.17
9/19	3	19	6.30	7.81	22.60	35.69	19.79	66.30	279.82

Note: Coll. = collection. Habitats are labeled as: 1= Potomac, 2= Rappahannock, 3= York, 4= Island, 5= Eastern Shore. Observations in station 2* are mean values from three stations in the river mouths.

APPENDIX IV- 2001 WATER CHEMISTRY [Me/Ca] DATA

Coll. date	Habitat	Station	[Mg/Ca] mol/mol	[Mn/Ca] umol/mol	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mol	[La/Ca] nmol/mol
7/10	4	4	4.45	3.81	11.23	29.03	9.99
7/10	4	5	4.20	1.07	6.29	44.79	4.34
7/10	4	29	4.44	1.67	6.84	47.59	4.37
7/10	4	30	4.35	2.99	7.36	49.63	4.81
7/10	4	33	4.23	2.35	6.43	57.92	6.99
7/11	5	25	4.26	2.81	6.47	31.89	8.08
7/11	5	27	4.69	8.49	7.02	51.99	6.11
7/11	5	28	4.23	8.35	6.21	45.76	10.98
7/13	1	9	4.26	0.75	6.73	47.93	2.34
7/13	1	10	4.26	0.61	6.74	42.15	2.18
7/13	1	11	4.29	0.49	6.40	39.67	1.85
7/13	1	2*	4.25	0.31	6.38	66.04	1.96
7/13	2	12	4.65	1.66	8.63	57.80	3.77
7/13	2	13	4.28	1.62	6.75	32.95	2.55
7/13	2	16	4.31	5.37	7.40	35.81	3.43
7/13	2	2*	4.27	0.34	6.66	47.93	2.18
7/16	3	17	4.20	0.27	7.19	29.49	3.52
7/16	3	18	4.37		6.16	27.64	8.51
7/16	3	19	4.64	5.48	4.92	43.55	4.35
7/16	3	2*	4.38	2.32	6.83	29.89	2.92
7/23	5	25	4.37	2.14	7.54	45.98	5.53
7/23	5	27	4.37	48.05	7.48	59.68	16.05
7/23	5	28	4.32	3.95	7.33	54.13	7.20
7/25	2	12	4.41	2.79	8.09	47.73	3.66
7/25	2	13	4.52	1.62	7.54	44.97	3.51
7/25	2	16	4.17	2.88	6.77	35.27	3.42
7/25	2	2*	4.48	0.61	7.71	51.86	3.20
7/25	3	17	4.47	4.65	7.18	32.63	4.20
7/25	3	18	4.24	19.67	8.09	39.13	8.31
7/25	3	19	4.07	5.24	6.75	29.66	3.48
7/25	3	2*	4.48	1.63	6.96	30.09	3.39
7/26	1	9	4.35	0.66	6.82	48.69	4.79
7/26	1	10	4.21	1.36	6.61	40.89	3.31
7/26	1	11	4.42	0.77	8.05	39.38	3.91
7/26	1	2*	4.24	0.22	7.03	65.98	2.74
7/27	4	4	4.35	1.05	7.99	75.04	6.31
7/27	4	5	4.53	0.76	6.55	39.81	4.30
7/27	4	29	4.20	1.11	7.42	51.04	6.02
7/27	4	30	4.33	0.89	6.75	52.94	5.29
7/27	4	31	4.26	3.34	7.55	57.84	6.52
7/27	4	33	4.21	2.20	7.00	61.62	5.29
8/6	2	12	4.80	4.67	9.83	61.27	4.95
8/6	2	13	4.94	2.34	9.11	42.46	3.02
8/6	2	16	4.33	0.72	12.61	56.36	4.19
8/6	3	17	4.75	7.31	7.89	32.84	3.24
8/6	3	19	4.68	1.59	8.68	32.41	4.56
8/6	3	2*	4.48	1.63	8.57	32.53	3.49

APPENDIX IV "Continued"

Coll. date	Habitat	Station	[Mg/Ca] mol/mol	[Mn/Ca] umol/mol	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mol	[La/Ca] nmol/mol
8/7	1	9	4.56	1.90	9.68	65.48	5.30
8/7	1	10	4.43	1.21	7.91	52.10	4.23
8/7	1	11	4.47	0.71	8.75	47.81	2.36
8/7	1	2*	4.60	0.77	8.45	76.23	2.51
8/7	2	2*	4.55	0.25	9.09	57.86	2.66
8/8	5	25	4.76	2.26	8.26	44.14	3.80
8/8	5	27	4.87	7.84	11.13	75.37	4.67
8/8	5	28	5.03	10.76	9.44	63.22	4.79
8/9	4	4	4.27	2.15	9.91	80.84	4.33
8/9	4	5	4.60	2.27	7.72	52.36	3.86
8/9	4	30	4.34	1.75	7.42	52.00	3.21
8/9	4	31	4.62	2.53	9.25	61.17	4.26
8/9	4	33	4.83	1.40	9.43	79.15	4.44
8/20	4	4	4.81	1.27	8.35	75.21	3.16
8/20	4	5	4.62	1.73	9.30	61.12	3.77
8/20	4	29	4.31	0.73	8.69	55.13	2.79
8/20	4	30	4.65	5.49	9.63	66.58	3.72
8/20	4	31	4.31	2.41	7.88	54.94	3.29
8/20	4	33	4.51	1.06	7.37	63.80	2.74
8/21	5	25	4.34	8.41	9.43	50.55	6.03
8/21	5	27	4.55	5.29	9.54	58.86	3.50
8/21	5	28	4.40	8.34	8.11	52.21	8.18
8/22	1	9	4.53	0.61	8.21	58.21	2.30
8/22	1	10	4.43	0.98	7.44	47.94	2.60
8/22	1	11	4.60	0.93	8.01	45.71	2.58
8/22	2	12	4.35	2.63	7.46	43.31	2.31
8/22	2	13	4.53	1.03	8.91	37.33	2.52
8/22	2	16	4.72	6.34	11.02	49.75	3.29
8/23	3	17	4.29	3.55	6.78	28.69	1.97
8/23	3	18	4.60	0.82	7.48	27.98	1.76
8/23	3	19	5.02	0.34	23.48	94.81	5.37
9/4	4	4	4.37	0.63	7.33	68.41	3.03
9/4	4	5	4.64	1.92	9.08	55.19	3.54
9/4	4	29	4.40	0.62	8.11	52.76	2.25
9/4	4	30	4.71	4.71	8.19	63.77	3.64
9/4	4	31	4.76	2.51	10.75	89.21	7.13
9/4	4	33	5.03	1.63	9.95	87.45	5.54
9/5	5	25	5.05	1.91	10.50	51.26	4.81
9/5	5	27	4.84	7.94	10.35	69.65	13.13
9/5	5	28	4.39	3.08	7.80	57.42	7.29
9/7	1	9	5.01	0.56	9.21	59.95	2.32
9/7	1	10	4.74	0.46	9.44	58.72	2.72
9/7	1	11	4.77	0.51	8.64	50.28	2.26
9/7	2	12	4.73	2.81	9.33	51.25	3.31
9/7	2	13	5.12	1.96	9.66	47.45	3.52
9/7	2	16	4.76	2.74	9.82	40.84	3.35
9/7	3	17	4.82	1.64	9.11	38.62	3.15

APPENDIX IV "Continued"

Coll. date	Habitat	Station	[Mg/Ca] mol/mol	[Mn/Ca] umol/mol	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mol	[La/Ca] nmol/mol
9/7	3	18	5.10	1.72	11.95	47.64	3.89
9/7	3	19	4.82	2.11	9.75	39.63	3.57
9/17	4	5	4.35	0.54	7.91	56.99	3.83
9/17	4	29	4.96	0.64	9.61	59.57	3.82
9/17	4	30	4.43	0.88	8.05	51.80	3.43
9/17	4	31	4.74	3.16	9.92	76.31	6.43
9/17	4	33	4.51	1.06	8.06	59.50	4.25
9/18	1	9	4.91	1.10	8.78	56.77	4.12
9/18	1	10	5.11	0.54	9.46	53.70	3.92
9/18	5	25	4.77	2.88	8.74	49.69	9.13
9/18	5	27	4.98	2.86	9.64	61.02	8.19
9/18	5	28	5.17	5.90	10.24	68.80	10.20
9/19	1	11	4.94	0.65	9.40	57.13	3.84
9/19	2	12	4.60	10.23	7.67	47.28	3.90
9/19	2	13	4.81	1.56	8.79	42.41	3.89
9/19	3	17	4.50	6.31	8.96	35.26	19.14
9/19	3	18	4.71	1.65	9.37	36.76	10.43
9/19	3	19	4.80	2.66	8.92	37.65	21.60

Note: Coll. = collection

APPENDIX V "Continued"

Catch date	Hab	Stat	SL mm	OTW mg/L	$\delta^{13}C$	$\delta^{18}O$	[Mg/Ca] umol/mol	[Mn/Ca] umol/mo	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mo	[La/Ca] pmol/mol
9/17	4	30	40.05	2.05	-4.55	-4.06	270.09	17.54	2.07	18.33	88.85
9/17	4	30	59.35	5.08	-3.87	-4.26	238.49	17.26	1.65	10.77	53.32
9/4	4	5	26.10	0.56	-3.17	-4.58	360.80	29.69	1.94	20.49	80.08
9/4	4	5	26.30	0.49	-3.37	-4.48	400.22	28.24	2.06	22.03	114.27
9/4	4	29	18.00	0.21	-4.66	-4.85		28.27	2.07	19.70	87.44
9/4	4	29	20.15	0.27	-4.65	-4.66		29.58	2.11	19.65	67.21
9/4	4	29	22.35	0.61	-4.11	-4.68	362.98	23.99	1.97	21.11	85.83
9/4	4	29	22.70	0.38	-3.49	-4.53	328.77	32.98	2.05	20.84	53.32
9/4	4	29	26.70	0.63	-3.35	-4.63	299.31	27.07	1.97	20.29	96.53
9/4	4	29	29.90	0.73	-3.28	-4.68	353.60	22.74	1.92	27.57	117.77
9/4	4	29	30.20	0.98	-3.52	-4.64	298.59	22.07	1.97	32.71	119.27
9/4	4	30	28.10	0.60	-2.75	-4.55	277.91	34.43	2.00	14.53	
9/18	5	25	39.99	1.78	-2.44	-3.40	232.27	22.68	1.99	12.14	68.28
9/18	5	25	43.39	2.01	-2.79	-3.75	244.90	16.05	2.18	15.71	75.74
9/18	5	27	36.30	1.56	-3.66	-3.77	247.38	35.41	2.02	14.71	77.72
9/18	5	27	36.46	1.45	-3.86	-3.67	277.44	27.31	1.84	8.63	48.53
9/18	5	27	38.11	1.64	-3.86	-3.52	265.16	34.37	2.18	17.33	85.78
9/18	5	27	40.53	2.11	-3.62	-3.52	230.26	31.56	1.87	14.50	81.59
9/18	5	27	50.16	3.55	-3.45	-3.57	219.52	35.98	1.83	15.68	70.97
9/18	5	27	50.23	3.06	-2.74	-3.73	207.00	24.42	1.89	8.86	47.18
9/18	5	28	36.11	1.37	-4.12	-4.63	249.66	44.71	2.05	16.51	82.08
9/18	5	28	43.59	2.44	-2.97	-4.08	274.69	45.16	2.43	24.15	125.70
9/18	5	28	46.59	2.77	-2.79	-3.48	249.53	51.68	2.15	19.50	93.81
9/18	5	28	55.26	4.17	-2.28	-3.17	235.34	34.11	2.02	15.49	85.32
9/18	5	28	61.88	5.93	-2.60	-3.27	226.67	51.89	2.23	13.33	69.57
9/5	5	27	22.51	0.42	-4.49	-4.50	362.33	33.66	1.97	13.61	61.60
9/5	5	27	29.13	0.70	-3.69	-4.56	337.38	30.99	1.62	7.90	38.89
9/5	5	27	34.40	1.15	-4.21	-4.49	363.57	31.91	1.84	12.32	70.70
9/5	5	27	35.11	1.12	-4.13	-4.10	364.09	28.33	1.87	11.07	68.25
9/5	5	27	50.96	2.84	-3.39	-4.36	309.37	42.06	1.80	9.33	57.89
9/5	5	28	20.59	0.25	-4.16	-4.00	346.21	57.34	2.06	15.34	49.69
9/5	5	28	25.37	0.55	-3.37	-3.97	288.58	56.06	2.10	19.99	87.81
9/5	5	28	28.08	0.72	-4.49	-4.50	323.31	67.08	2.08	17.44	101.01
9/5	5	28	33.10	1.03	-2.72	-3.76	354.50	69.01	2.16	21.51	98.71
9/5	5	28	34.52	1.11	-3.17	-3.91	322.94	55.92	1.96	13.60	93.81
9/5	5	28	36.67	1.36	-3.54	-3.69	309.60	44.46	2.13	15.73	87.10

Note: Hab = Habitat , 1=Potomac, 2= Rappahannock, 3= York,, 4= Island, 5 = Pocomoke.
.Stat =station , Sl = fish standard length, OTW= otolith weight.

APPENDIX V- 2001 FISH AND OTOLITH MICROCHEMISTRY DATA

Catch date	Hab	Stat	SL mm	OTW mg/L	$\delta^{13}C$	$\delta^{18}O$	[Mg/Ca] umol/mol	[Mn/Ca] umol/mo	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mo	[La/Ca] pmol/mol
8/22	1	11	35.80	1.27	-2.66	-5.04	321.35	25.34	2.17	45.54	210.75
8/22	1	11	39.91	1.33	-2.68	-5.07	289.52	24.64	2.21	31.19	142.36
8/22	1	11	41.00	1.68	-2.66	-5.18	339.08	37.91	2.03	31.59	229.56
9/19	1	9	24.82	0.49	-2.97	-4.08	361.97	22.09	2.00	25.12	118.82
9/19	1	9	31.97	1.14	-2.71	-4.14	281.94	22.61	2.19	27.32	125.43
9/19	1	9	39.98	1.93	-2.92	-4.19	250.36	21.84	2.28	30.06	139.45
9/19	1	9	46.64	2.69			234.39	16.30	1.93	21.17	92.92
9/19	1		52.28	3.68	-3.39	-4.07	249.44	21.74	1.75	16.14	85.51
9/19	1		56.23	4.10	-1.61	-4.16	252.48	17.23	2.21	24.61	106.12
9/19	1		63.55	5.86	-2.84	-3.61	227.08	17.54	2.29	29.47	109.75
9/7	1	9	23.75	0.38	-3.63	-4.79	389.32	36.54	2.05	17.27	77.31
9/7	1	9	27.02	0.61	-3.27	-4.81	300.90	35.72	2.09	18.66	76.62
9/7	1	9	28.15	0.71	-3.44	-5.12	336.00	29.63	1.99	15.57	59.07
9/7	1	9	28.59	0.65	-3.14	-5.08	257.81	25.38	1.95	14.81	71.24
9/7	1	9	30.81	0.82	-3.33	-4.79	290.83	24.51	2.02	17.33	100.16
9/7	1	9	33.09	0.94	-3.16	-4.95	271.61	28.31	2.13	21.11	80.66
9/7	1	9	35.01	1.16	-2.60	-3.27	313.50	33.23	2.03	17.22	86.67
9/7	1	9	35.05	1.20	-3.56	-4.79	287.29	29.51	1.62	8.61	46.07
9/7	1	9	35.73	1.20	-3.26	-4.93	312.32	29.32	2.28	23.19	259.94
9/7	1	10	29.34	0.70	-2.72	-4.92	326.27	16.98	2.11	20.36	85.20
9/7	1	10	30.01	0.76	-3.44	-4.77	298.69	30.62	2.06	22.42	91.11
9/7	1	10	34.14	1.10	-3.23	-4.71	347.20	27.88	2.21	28.23	132.88
9/7	1	11	20.88	0.29	-3.43	-4.76	328.98	18.93	2.13	22.21	60.26
9/7	1	11	21.38	0.33	-3.31	-4.60	389.14	23.20	2.07	23.20	88.57
9/7	1	11	26.77	0.60	-2.85	-4.55	352.97	20.67	2.16	24.88	103.59
9/7	1	11	26.92	0.59	-2.57	-4.73	348.61	25.88	1.92	24.72	110.42
9/7	1	11	28.20	0.71	-3.11	-4.63	348.54	19.17	1.91	17.82	66.68
9/7	2	12	64.29	5.97	-2.34	-4.60	200.32	28.54	1.46	1.95	13.96
9/7	2	16	36.54	1.40	-3.60	-3.95	306.62	32.50	1.90	11.52	66.42
9/19	2		33.12	1.10	-3.46	-4.13	287.27	21.81	1.56	13.00	64.55
9/19	2		39.19	1.75	-3.39	-4.07	241.91	32.63	1.85	18.85	90.11
9/19	2		32.99	1.09	-1.68	-3.75	252.29	22.15	2.13	19.37	92.04
9/21	3	19	29.75	0.86	-2.21	-3.41	256.37	16.20	2.06	10.88	55.91
9/21	3	19	41.89	1.93	-2.46	-3.51	215.15	20.48	1.84	8.60	46.12
9/6	3	17	15.17	0.13	-4.61	-4.53	327.59	21.00	2.08	8.09	22.10
9/6	3	17	16.02	0.07	-4.48	-4.27	330.92	20.24	2.09	7.45	65.75
9/6	3	17	18.22	0.20	-3.37	-3.90	384.65	25.84	1.94	11.76	49.97
9/6	3	17	20.33	0.29	-3.51	-4.02	316.12	25.03	1.89	8.66	61.35
9/6	3	17	35.74	1.31	-2.84	-3.61	268.40	20.90	2.05	14.27	68.82
9/6	3	18	23.35	0.44	-3.64	-3.76	340.17	28.71	2.22	10.59	44.42
9/6	3	19	16.36	0.15	-4.22	-4.21	380.24	16.86	2.09	9.72	
9/30	4		48.49	2.96	-3.59	-3.22	218.20	13.68	1.62	39.89	184.64
9/30	4		48.22	3.42	-1.63	-2.91	243.02	29.38	1.87	21.17	109.21
9/30	4		58.82	5.62	-2.27	-3.54	184.36	15.61	1.95	24.88	99.95
9/14	4	33	29.50	0.72	-4.09	-5.17	297.28	24.71	2.09	25.04	99.50
9/14	4	33	44.25	2.20	-4.19	-5.04	273.37	28.27	2.00	18.94	99.12
9/17	4	5	47.25	2.75	-2.80	-3.82	279.38	30.78	1.94	16.03	78.36

APPENDIX VI- 1998 FISH AND OTOLITH MICROCHEMISTRY DATA.

Catch date	Hab	Stat	SL mm	OTW mg	[Mn/Ca] umol/mol	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mol	[La/Ca] pmol/mol
9/24	1	11	34	1.46	18.87	2.05	34.61	151.85
9/24	1	21	46	2.88	19.05	1.94	31.85	139.31
9/24	1	21	59	3.36	11.80	1.83	31.57	141.38
9/24	1	21	60	5.46	13.73	2.00	30.42	241.41
9/24	1	24	36	1.25	21.76	1.89	35.55	118.37
9/24	1	24	57	4.59	11.19	1.99	44.76	264.90
9/24	1	24	58	4.79	14.38	1.76	35.40	240.67
9/24	1	24	60	5.74	21.76	2.12	28.58	136.84
9/24	1	26	23	0.44	18.31	1.93	30.37	150.29
8/19	2	1	37	2.52	49.20	2.19	34.80	145.20
8/19	2	20	46	2.60	17.22	2.18	50.46	198.39
8/19	2	25	36	1.71	20.50	2.26	30.69	123.66
8/19	2	33	38	1.90	21.59	2.09	21.69	78.27
8/19	2	35	35	1.26	32.68	2.32	27.25	209.76
8/19	2	40	36	1.57	19.76	1.84	14.16	40.11
8/19	2	50	31	1.20	36.86	2.18	30.18	131.49
9/25	2	32	52	3.72	18.33	1.82	29.37	99.07
8/20	3	8	40	2.41	18.04	1.72	16.51	65.17
8/20	3	36	37	1.47	16.59	1.89	16.89	134.09
8/20	3	36	50	3.36	21.64	2.03	12.38	65.95
9/22	3	2	44	2.63	11.13	1.94	37.86	127.65
9/22	3	2	45	2.67	13.61	2.00	47.96	145.52
9/22	3	2	49	4.02	10.23	1.93	32.87	190.39
9/22	3	2	57	4.29	15.90	1.88	34.49	258.27
8/18	4	1	32	0.92	22.41	2.01	26.13	100.82
8/18	4	1	42	2.19	21.52	1.99	20.79	149.83
8/18	4	8	23	0.51	24.27	2.13	27.57	255.14
8/18	4	8	30	1.08	23.59	2.10	39.31	151.37
8/18	4	31	25	0.57	26.83	1.90	28.57	261.35
8/18	4	31	28	0.72	22.52	1.97	25.50	237.83
8/18	4	31	37	1.81	22.36	2.05	27.56	107.24
8/18	4	31	57	4.14	22.20	1.99	12.45	105.00
8/18	4	35	23	0.47	23.02	2.11	34.46	297.97
8/18	4	35	26	0.70	28.24	2.47	44.15	166.98
9/24	4	3	41	2.43	14.00	1.71	22.27	80.51
9/24	4	3		2.85	17.06	1.67	14.75	129.15
9/24	4	3	54	4.66	16.74	1.84	18.14	69.40
9/24	4	27	46	2.89	10.32	1.72	17.75	53.77
9/24	4	27	53	4.29	13.89	1.64	12.57	146.14
9/24	4	27	59	4.94	12.62	1.60	5.76	28.56
9/24	4	34	54	4.28	13.04	1.64	16.45	54.44
9/24	4	34	61	5.80	13.68	1.75	14.47	52.78
9/24	4	42	57	4.68	12.81	1.71	19.13	74.91
9/24	4	43	43	2.33	14.28	1.83	26.30	185.38
9/24	4	43	44	2.62	13.21	1.92	33.11	130.11

APPENDIX VI "Continued"

Catch date	Hab	Stat	SL mm	OTW mg	[Mn/Ca] umol/mol	[Sr/Ca] mmol/mol	[Ba/Ca] umol/mol	[La/Ca] pmol/mol
9/24	4	43	57	5.43	13.21	1.60	13.99	59.37
8/18	5	4	26	0.80	48.17	2.36	19.94	73.05
8/18	5	33	37	1.68	42.87	2.48	32.05	120.49
8/20	5	3	34	1.19	58.93	2.22	19.43	145.18
8/20	5	3	33	1.35	20.82	2.07	15.37	176.77
8/20	5	3	40	2.12	49.26	2.07	30.52	122.31
8/20	5	16	54	5.27	28.95	1.62	10.99	47.86
8/20	5	21	42	2.06	23.06	2.29	28.01	102.63
8/20	5	29	32	0.96	63.42	2.26	33.48	238.92
8/20	5	29	37	1.49	60.53	2.20	32.33	122.41
8/20	5	29	37	1.50	57.94	2.32	41.11	117.04
8/20	5	29	39	1.74	58.94	2.26	39.73	273.18
8/20	5	34	41	2.19	74.33	2.32	27.76	73.45
8/20	5	46	35	1.23	22.21	2.00	14.33	48.68
8/20	5	46	39	1.84	25.63	1.97	16.57	86.63
8/20	5	49	59	5.17	19.02	1.69	12.83	47.44
8/20	5	49	46	2.78	45.38	2.11	24.87	85.95
9/22	5	5	47	2.88	31.03	1.81	15.24	52.68
9/22	5	19	61	5.53	29.09	1.79	17.20	61.34
9/22	5	26	38	1.79	25.10	1.95	17.71	56.04
9/22	5	35	58	4.47	30.22	1.51	6.25	22.45
9/22	5	35	57	4.78	30.53	1.46	6.78	32.15
9/22	5	35	60	5.35	26.38	1.80	9.24	74.58
9/22	5	35	62	6.00	41.42	1.62	6.40	31.83
9/22	5	38	40	1.76	26.46	1.91	33.98	103.91
9/22	5	40	35	1.66	15.01	1.75	19.98	69.34
9/22	5	40	46	2.68	19.19	1.96	17.84	134.64
9/22	5	40	59	5.34	15.53	1.54	6.23	24.25
9/22	5	41	40	2.18	42.09	1.95	27.05	150.48
9/22	5	41	57	4.67	35.53	2.14	28.03	90.67
9/22	5	60	54	4.46	19.12	1.57	4.97	76.47
9/24	5	54	48	3.05	21.55	1.77	30.28	99.88

Note: Hab= habitats, 1= Potomac, 2 = Rappahannock, 3=York, 4= Island, 5= Pocomoke, Stat = Station, SL= fish standard length, OTW= otolith weight .

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