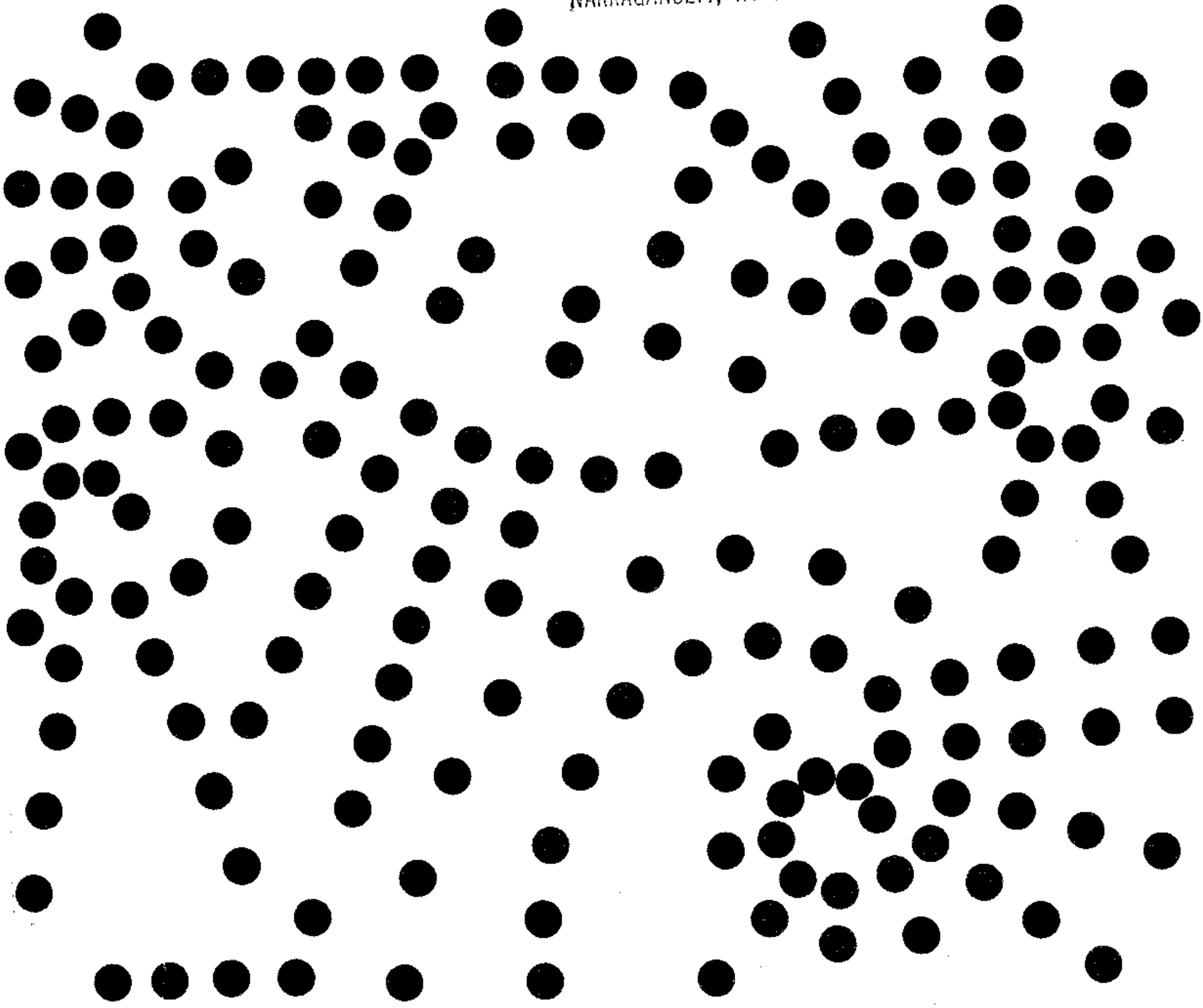
INDUSTRIAL PROSPECTS FOR CHITIN AND PROTEIN FROM SHELLFISH WASTES

MIT Sea Grant Program
Massachusetts
Institute of Technology

A Report on the First Marine Industries
Business Strategy Program
Marine Industry Advisory Service



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MIT Sea Grant Program
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The MIT Sea Grant Program's Marine Industry Advisory Service, of which the Marine Industries Business Strategy Program and the MIT/Marine Industry Collegium are part, seeks to advance industry's uses of the seas through a mutually beneficial partnership between Sea Grant and companies of national and international stature. Through the Marine Industry Advisory Service, Sea Grant affords industry direct access to university-based knowledge that member companies can use to make sound, profitable business decisions in the oceans.

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We hope the report reflects clearly the important contributions of our industrial partners, but we are responsible for the conclusions.

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EXECUTIVE SUMMARY

Although chitin and derivatives of chitin have been studied for many years, and although their many intriguing chemical properties have also been known for years, commercial utilization has been almost nonexistent. A key problem has been that potential users have been reluctant to commit capital to development of chitin applications because the supply has been uncertain and the costs have been high in experimental quantities. In turn, potential suppliers of chitin have been reluctant to invest in production facilities in the absence of known markets for using chitin.

This study was designed to address the industrial prospects for utilization of chitin (and its derivatives). As the title suggests a business strategy involving both chitin and protein from shellfish has been developed and evaluated. The strategy appears to offer a rational and profitable way to resolve the dilemma by treating chitin as a by-product of a protein recovery process that, in some cases, may be profitable even in the complete absence of any markets for the chitin. This strategy should assure availability of dried shell waste in sufficient quantities to make possible production of chitin in amounts needed to supply initial markets.

Likely markets are proposed based on an extensive analysis of the literature of chitin applications and markets for similar chemicals. Promising areas for further research and development are suggested.

Overall Conclusion

It appears to be commercially feasible to produce between one and four million pounds of chitin/chitosan per year for sale at a price between $1.00 and $2.50 per pound. For both technical and economic reasons, the most effective business plan would be for certain strategically located shellfish (or food waste) processors to reduce shell waste to two dried components; (1) a mechanically separated protein for use in animal feed, and (2) the remainder of the shell waste* for sale to a regional or national producer of chitin derivatives. Such an arrangement would solve many processors' waste problem, and probably at a reasonable profit considering all credits, without requiring them to enter fields far outside their present expertise. It would also provide a larger aggregate supply of chitinous shell residual to a chemical processor whose capabilities are more certain to include appropriate process, product, and market development capabilities.

Chitin Technology

Chitin is a straight chain polysaccharide polymer of N-acetyl glucosamine, closely related to cellulose. Its most important derivative at present, chitosan, is essentially polyglucosamine. Chitosan possesses a high density of amino groups per unit weight. Under acidic conditions chitosan carries a strong positive charge and is water-soluble. Under neutral or basic conditions, the many uncharged amino groups give chitosan a high capacity for binding transition metal ions by chelation.

Properties of chitosan important for selected groups of commercial applications are:

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*designated *shell waste residual*

Property	*Applications*
High charge density and potential binding capacity (relative to other substituted celluloses)	Ion-exchange or chelating solids for chromatography, metal recovery from waste streams, industrial process water purification for recycling, etc.
Film-forming	Ion-exchange membranes for electrodialysis
Coagulation	Waste water treatment
Strong binding to negatively-charged polymeric products	Paper-strength additive, dye binder for textiles, binding agent for non-woven fabrics, sausage-casing component, adhesives
Wound-healing promotion, nonthrombogenic	Wound treatments, surgical adjuncts

A substantial number of chitin derivatives other than chitosan have been prepared and additional derivatives are clearly possible.

Supply

Production of by-product protein makes an important contribution to the economic viability of chitosan production. Under an optimistic set of assumptions about protein price, the initial mechanical separation of protein from shell can yield a sufficient return to justify investment without any contribution of revenue from further process steps. Under a more pessimistic set of assumptions, the sale of protein is nevertheless important in reducing the minimum required price of chitosan.

The most viable industrial organizational schema is a two-step production sequence:

- Local production of dried protein and shell waste residual by large or centrally located shellfish processors, drawing shell waste from their own operations and (possibly) from other shellfish processors within a 50-mile radius.
- Shipment of dried shell waste residual to a regional or national chemical industry plant for production of chitosan.

Chitosan production of between one and four million pounds per year from shellfish wastes is likely to be feasible with a minimum anticipated price of chitosan between $1.00 and $2.50 per pound. If demand for chitosan exceeds the one to four million pound per year range and is capable of supporting higher chitosan prices, sources of chitin other than shellfish waste may be brought into production. The most likely of these other sources are fungal waste by-products from citric acid and other industrial fermentations.

Demand

Based on comparisons with sales volumes and prices of cellulosic polymers related to chitosan, there appears to be a reasonable expectation that the market can absorb several million pounds of chitosan at prices between $1.60–$1.90 per pound.

Selected special properties of chitosan may allow it to achieve significant sales levels at prices higher than the $1.60–$1.90/lb range suggested by the comparison with general cellulosics:

- *Ion-exchange resins* may alone be a multimillion pound market for chitosan. Comparisons with existing commercial weak-base ion exchangers suggest that, on the basis of equal binding capacity, chitosan may be able to sell for between \$2.35–\$6.40 per pound.
- *Coagulation applications* in wastewater treatment in Japan absorb about 1.3 million pounds of chitosan per year at a selling price of between \$2.12 and \$2.72 per pound (1976). U.S. trials of chitosan coagulation treatments of various food processing wastes have yielded favorable results as compared with competing polymers selling in the range of between \$1.50 to \$3.00 per pound.
- *Film and fiber applications*, despite considerable long-term interest, have technical characteristics as yet too poorly defined for meaningful market appraisals to be made.
- *Paper and pulp applications* under reasonable, but highly speculative, assumptions may be capable of utilizing on the order of a million pounds of chitosan at a price of approximately \$2.00/pound after further development research has been performed.
- *Wound healing accelerators and temporary prostheses* are application areas with potentially high value per pound but relatively small volume.

1 INTRODUCTION

Chitin is a natural carbohydrate polymer that occurs primarily as a structural constituent in the shells of crustaceans and insects, and to a lesser extent in other plant and animal forms. It is a close chemical relative of cellulose, and, like cellulose, can be modified both chemically and physically to produce materials with a wide variety of potentially useful properties. Several times over the last 40 years these properties — the abundance of chitin in nature, and the prospect of converting shellfish waste into a valuable resource — have stimulated the interest of entrepreneurs, government agencies concerned with exploitation of the oceans, and academic researchers. However, for all the effort, little sustained production and use of chitin has taken place. The successive waves of interest have yielded a considerable amount of technical literature and patents for numerous types of applications, but less effort appears to have been devoted — especially by the public sector — to understanding the economic questions relevant to chitin development.[a]

This report is intended to fill part of that void by identifying areas of technical and business uncertainty whose resolution will be important for chitin production and utilization on a commercial scale. In this study, we have assembled and organized fundamental data, created a mode of analysis whose purpose is to clarify reasonable economic expectations, and assessed the practicality of specific, alternative business situations.

Section 2, "Chitin Technology," begins with a basic description of the chemical and physical properties of the major chitin derivatives that have been studied. After fundamental properties are catalogued, we explore the implications of some particular properties for selected groups of potential applications.

In Section 3, we suggest a two-step process for utilization of the wastes. First, individual large shellfish producers and groups of small producers in close proximity could use a mechanical process to separate loosely-bound adherent protein for drying and sale as an animal feed component. The shell waste residual could then either be discarded[b] or sold to a national or regional plant for the production of chitin derivatives. This two-step process is favored because of probable economies of scale in a central chitin derivative plant and because of observed reluctance among shellfish processors to consider entering the unfamiliar territory of the fine chemicals business.

We address the question, "How much protein and chitin derivative can be produced from the shellfish waste in different areas at what cost?" From published data, and from conversations with individuals in contact with shellfish harvesting and processing practices in different localities, we estimate the quantities of particular kinds of shellfish waste likely to be available in different areas. Given this basic process and numerous assumptions about waste composition and various components of production cost, we first estimate the price that would have to be paid by the chitin derivative plant for the shell waste residual to induce various levels of its production in different areas. Then we estimate the price of the ultimate chitin derivative that would allow the chitin derivative plant to pay those prices. In doing this, we use two sets of assumptions — one believed to be more optimistic and one less optimistic than we expect — to generate a reasonable range of estimates for the long-run supply of chitin derivative. Possible

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[a] Exceptions are the Environmental Protection Agency funded feasibility study by CRESA of possible chitin production in Alaska[1], and the purchase by the National Oceanographic and Atmospheric Administration of initial production of developmental quantities of chitin in the state of Washington.

[b] Under some conditions (including favorable protein prices) the production of protein by itself may be sufficiently profitable to justify the required investment.

sources of chitin other than shellfish waste are also briefly examined.

Section 4, "Analysis of Possible Demand," addresses the question, "How much chitin derivative will be bought at different prices?" Two approaches are used to obtain a proven estimate of likely demand. One approach is to examine the general relationship between price and quantity sold for polymer products whose markets may be expected (on chemical or functional grounds) to have some similarity to the markets for chitin derivatives. The second approach is to examine the market potential of a few specific applications where there is reason to expect that chitin derivatives can perform technical functions competitive with existing materials.

The conclusion section is divided into three parts, each of which distills from our analysis the points of likely interest to a particular group of individuals. The first subsection of conclusions addresses interests of the business community, outlining the present state of our information on the opportunities for commercial utilization of shellfish wastes. The second subsection of conclusions outlines areas that appear to be most promising for applied researchers, and government agencies interested in funding applied researchers. The third subsection outlines interesting areas for basic research that may lead to useful innovations.

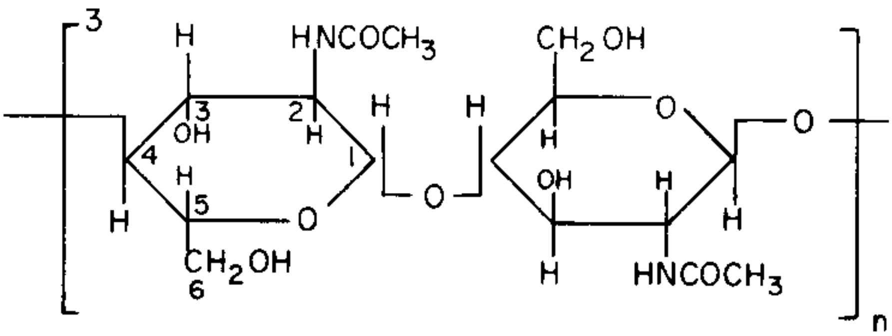
REFERENCE

1. CRESA (a consulting firm). "Pollution Abatement and By Product Recovery in Shellfish and Fisheries Processing." Environmental Protection Agency, Water Pollution Control Research Series, Project #12130FJQ (1971).

2 CHITIN TECHNOLOGY

2.1 General Description and Chemical Properties

Chitin is a long straight chain polymer of N-acetyl-glucosamine whose units are linked by β(1→4) bonds. It may be regarded as a derivative of cellulose in which each C-2 hydroxyl has been substituted by an acetylamino group, $-NHCOCH_3$.



Chitin is a white solid, generally possessing some degree of crystallinity. Differences in the complex structures of the different species and tissues in which it is found may account for differences in chain length, crystallinity, and departures from complete acetylation of all the amino groups. While it occurs in relatively pure form in special instances,[a] the process of separating it chemically from the other complex organic and mineral substances with which it is most commonly associated imposes some risk of modification, and raises some uncertainty as to the precise identity of the chitin polymer in different species. Rarely, as in the case of the fungus *Mucor Rouxii*,[28] chitin occurs predominantly in its deacetylated form, which is known as chitosan. More subtle crystal structure differences occur in other organisms, but the chitin that is found in shrimp, crab, and lobster shells is generally thought to be for practical purposes the same chemical entity — differing chiefly in its association with other shell constituents.

Chitin is insoluble in water, dilute acids, cold alkalis, or organic solvents. Unlike cellulose, it is also insoluble in Schweitzer's (cuprammonium) reagent. It is soluble in certain hot concentrated neutral salts such as lithium thiocyanate or lithium oxide, or in hexafluoroisopropanol or hexafluoroacetone sesquihydrate[2]. Other more complex solvent systems, such as trichloroacetic acid with methylene chloride and chloral hydrate have been reported,[25] and still others may yet be developed.

Chitin may be swollen in cold alkali suspension; in this process some free hydrogens are replaced by the alkali cation (e.g., Na^+ in NaOH) and some deacetylation occurs. However, most of the swelling is due to spreading of the interchain structure. Repeated freezing in alkali suspension causes dissolution, but the regenerated chitin is still insoluble in water. After a simple swelling treatment in caustic[b], chitin can be solubilized as a true xanthate with carbon disulfide and reprecipitated as a filament or film in the manner of viscose rayon. Similar treatments have been directly applied to shrimp shell, finely divided, and stirred in 35–40% NaOH and crushed ice to achieve a degree of substitution of 0.5.[c,12] Chitin may also be swollen in dimeth-

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[a] For example, as fibrous pediments on the marine diatoms, *Thalassiosira fluviatilis* and *Cyclotella cryptica*.[1]

[b] Either 2 hrs. at room temperature in 50% NaOH or 2 hrs. at 0° C in 35% NaOH. (See also ref. 29).

[c] That is, .5 xanthate groups per sugar residue, on the average.

ylsulfoxide, yielding a good preparation for subsequent treatments to produce derivatives such as carboxymethyl or hydroxyethyl chitin. (See Derivatives, 2.2.3 below.)

More drastic treatments resulting in swelling or in solution of chitin induce hydrolysis and may result in more or less complete break-up of the polymer. Prolonged heating in concentrated acids may remove the acetyl groups and break the chains into pure glucosamine. Treatment in hot alkalis also removes acetyl groups, but can be controlled to minimize chain breakage. This selective hydrolysis produces chitosan, a deacetylated chitin derivative, which is soluble in weak solutions of most acids, and whose outstanding properties give it special rank in the list of potentially useful derivatives. (See Section 2.2, below).

2.2 Properties and Capabilities Related to Applications (for Structure and Solubilization, see Section 2.1, above)

2.2.1 Stability, Physiological Compatibility, Films and Fibers, etc.

Chitin is a stable compound, generally resistant to attack. However, it is enzymatically biodegradable by some organisms, including humans.[d] In pure form, it is not antigenic in mammalian test systems, but has been observed to elicit an immune response if not thoroughly purified of its naturally associated protein.

When dissolved in the special solvents mentioned in section 2.1, it can be regenerated, extruded, or cast in the form of filaments or sheets. Films cast on metal from 2% solutions in hexafluoroisopropanol or 1.4% solutions in hexafluoroacetone sesquihydrate are reported[2] as tough, transparent, nontacky, flexible, quite pliable when hydrated, and stable in water, but degradable by lysozyme. Filaments obtained from anhydrous trichloroacetic acid solvent systems by extrusion into nonsolvents such as acetone and then neutralized in KOH and 2-propanol, have developed high tensile strengths when prestretched. Filaments obtained from xanthates by extrusion into an acid regenerating bath[e] have been reported as "soft,"[13] and it would be interesting to determine whether prestretching might also induce a higher tensile strength, perhaps by unfolding slightly kinked polymer chains, or by extruding trapped water, allowing closer interaction between adjacent polymer chains. Such soft filaments have been strengthened by coprecipitation with cellulose from a mixed xanthate solution.

2.2.2 Chemical Modifications — General

A number of chemical derivatives of chitin can be made that display different chemical and physical properties. In addition to the xanthates, these derivatives include chitosan (deacetylated chitin, or polyglucosamine), carboxymethyl chitin, hydroxyethyl chitin, ethyl chitin, chitin sulfate, glycol chitin, glucosylated chitin, nitrochitin, and a number of chitosan derivatives such as cyanoethylated chitosan. Still other derivative possibilities have yet to be explored. Since the amino group of chitosan can be reacted with nitrite to form a relatively stable diazonium ($-N = N^+$) intermediate, this intermediate could be used to couple a wide variety of aromatic groups to the chitosan polymer to produce novel derivatives with various properties.

2.2.3 Specific Derivatives

2.2.3.1 Chitosan This deacetylated form of chitin is the most familiar derivative, and is a cationic polyelectrolyte with one amino group and two free hydroxyls for each glucose ring. It is

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[d] Ref. 2. See also carboxymethyl chitin, Section 2.2.3, below)

[e] Milled chitin flakes steeped in caustic soda are pressed to remove excess NaOH, shredded, and stirred with cracked ice and CS_2 for 4 hrs. at 0° C or below. The resulting viscose solution may be extruded into a bath containing sulfuric acid and ammonium sulfate, or other acid/sulfate combinations.

insoluble in pure water but, unlike chitin, is soluble in weakly acidic aqueous media in which it is present as the acid salt. The pK_a[f] of the positively charged ammonium group is about 6.2. When the pH is raised above about 6.5, chitosan precipitates in the form of a gelatinous floc. In this process, fine particles of substances suspended in the medium are trapped in the precipitate, thus clarifying the remaining solution and leading to one major set of possible applications. The coagulation of suspended solids is particularly aided by the high density (one per sugar residue) of the amino groups on the chitosan molecule, each of which is a potential binding site for groups on the suspended particulate matter.

The same gelatinous chitosan precipitate has been proposed for use as a thickener, stabilizer or texture modifier in various consumer products that are now formulated with natural gums and starches. However, in this regard, it should be emphasized that chitosan is cationic (positively charged) in solution, while most other polymers with which it is compared are anionic (negatively charged).

Because of its cationic nature, chitosan spontaneously forms insoluble complexes with natural tannins, lignosulfonates, and other anionic polyelectrolytes, and can be used to recover or remove them from solution.[31] Thus, chitosan would also be incompatible in solution with most ionic water-soluble gums (including alginates, fucoidin, pectate, sulfated carageenan) as well as carboxymethyl cellulose and polyacrylates, since these are polyanionic. Since it is also insoluble in the presence of sulphuric acid or sulfates, it is similarly incompatible with sulfonated detergents. On the other hand, acid solutions of chitosan are compatible with nonionic water-soluble gums, starch, dextrins, glucose, sucrose, polyhydric alcohols (glycols, glycerol, sorbitol, etc.), oils, fats, waxes, and nonionic emulsifiers.[13]

Chitosan films may be cast on metal substrates from acidic solutions of chitosan and dried by heating. However, film studies have been hampered by variability in the qualities of starting material, especially that obtained from commercial sources. This is largely due to the lack of reliable quality control criteria, since the relationship between easily measured criteria such as viscosity, and the more difficult (and basically more important) ones such as molecular chain lengths are not yet scientifically determined. Chitosan films are tough, flexible, and transparent; they are about as water-permeable as cellophane, but are an effective CO_2 barrier, 100 times less permeable than cellophane. Their electrical conductivity is similar to that of organic molecular crystals. Physical studies of these films[3] suggest that the polymer inter-chain spacing is not rigid and that various substances can be inserted and held in the films, with the chain spacing adjusting to accommodate them. If so, this is likely to be an exploitable property by which conductivity, flexibility, and other characteristics might be manipulated.

Films can also be extruded from acid solutions of chitosan into a 70° C coagulating bath containing NaOH and sulfonic acid esters of high molecular weight alcohols.[14] Since chitosan more readily forms a xanthate with carbon disulfide than does chitin, extrusion into a regenerating bath provides an alternative method for producing films and filaments.[g] As with chitin, mixed xanthates have been prepared with cellulose,[18] but the superior ability of chitosan to bond ionically to cellulose results in a more intimate copolymer extrusion.

Chitosan is soluble in solutions as weak as 1% of acetic, formic, lactic, malic, malonic, propionic, or adipic acids. It will dissolve in 5% succinic acid and, at an acid concentration of 10%, is soluble in oxalic, citric, pyruvic, or tartaric acids. Some of these agents enjoy a large range of concentration tolerance, while others are narrower. Thus, formic acid is satisfactory in the entire range between 0.2 and 98%, while acetic is good only up to 50%. At the extremes of each range, the solutions will contain gel particles.[32]

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[f] The pK_a is the pH at which half of the nitrogen groups are present in the free amine ($-NH_2$) form and half are present in the charged ($-NH_3^+$) ammonium form.

[g] Acidic solutions of chitosan can be precipitated with excess alkali to give a final concentration of 15–20% alkali. The shredded, pressed chitosan cake can then be reacted with CS_2 in the same manner as alkali-treated chitin.

Inorganic acids, except for sulfuric and phosphoric, in concentrations around 1% will generally dissolve chitosan after prolonged stirring and warming. Solubility improves as chain length decreases, which sometimes occurs as a result of commercial methods for deacetylation in the production of chitosan.

A mixture of dimethylformamide and dinitrogen tetroxide is an excellent solvent for cellulose, chitosan, and several other marine polysaccharides, including algin, agar, laminarin, and the mucilage of *Ulva*. Highly ionic polymers like alginic acid, *Ulva* mucilage, and chitosan give nonviscous solutions in this solvent, owing perhaps to a slight amount of chain coiling.[33]

Good solubility and film-forming characteristics notwithstanding, the most noteworthy properties of chitosan are those related to its unusual charge density and its resultant molecular binding capabilities. These features are manifested in a powerful ability to capture certain metal ions from solution, to bind dyes, to serve as a chromatographic separator for biological macromolecules, to adhere strongly to glass, rubber, and many plastics as well as to cellulose and cellulose derivatives, and to form complexes with negatively charged molecules.

Chemically modified celluloses, such as aminoethyl cellulose, diethylaminoethyl cellulose, and para-amino benzyl cellulose are known as complexing agents for transition metals. Such materials contain a small number of amine groups compared to chitosan, because it is impossible to introduce synthetically more than 1.5% nitrogen into the cellulose chains, while chitosan contains up to 6.2%. Chitin, and especially chitosan, are excellent for capture or chelation of the transition elements (and certain posttransition metals such as arsenic) and it ably collects Hg, Zn, Tb, Ag, Sb, In, Au, Co, Cr, Ni, Al, and Cu in the presence of large concentrations of Na, K, Ca, and Mg salts as found in sea water. Collection can be performed by bulk adsorption in suspensions of chitosan[h], or often more efficiently in chromatographic columns. Since binding or elution may require acidification, it is convenient that chitosan's solubility in dilute mineral acids is insignificant at ambient temperatures. Its affinity for some metals such as molybdenum, copper, or mercury, is very high, requiring elution from columns by specially selected agents such as KCN or ammonium thiocyanate or other special measures. Its affinity for mercury is comparable to Dowex, but it should be noted that mercury is the metal most efficiently fixed by Dowex A-100, and that Dowex is heavier than chitosan, requiring more weight for any given column volume.[9]

Very little exploration of the utility of chitosan derivatives as ionic collectors has yet been attempted. However, it is appreciated that certain inorganic derivations could be useful, and can be produced by the natural affinity of anions for this polycation. Thus, oxyanions of metals, notably metavanadates, dichromates, molybdates, paramolybdates, or tungstates, should bind effectively to chitosan. Since chitosan polymolybdate is known to be stable, it should also be a good collector for phosphate by way of the well-known phosphate-molybdenum reaction. It is reported also that strontium is collected on chitosan polymolybdate as well as on chitosan polytungstate.

Because of its many side groups, including both hydroxyls and aminos, one would expect a considerable number of fortuitous affinities between chitosan and other macromolecules such as proteins and nucleic acids. Several instances of nonspecific binding are known, following the examples which make DEAE cellulose and other substituted celluloses so useful in the biochemistry laboratory. Tobacco mosaic virus (TMV), a protein-encapsulated organism, can be absorbed on chitosan from a 0.01 M phosphate buffer at pH6.8 and eluted without harm by K_2HPO_4 in the pH range between 7.2 and 7.7. Thyroglobulin has also been isolated by similar mild treatments[5], and other analogous possibilities no doubt exist. Solutions of chitosan mixed with suspensions of microcrystalline cellulose and dried in thin layers on glass plates have been useful for the separation of nucleic acid constituents.[26] One may anticipate that as chitosan be-

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[h] A modification of bulk adsorption is collection by precipitation of chitosan in solutions of the metals, either by adding NaOH or an excess of water. Chitosan precipitation occurs at a low enough pH to avoid coprecipitation of the metal hydroxide.

comes better known and available for chromatographic trials, other experimental separations will be reported.

Other binding phenomena are known, not related to chromatography so much as to applications in adhesives, coatings, dye mordants, and complexes with specially compatible solids. Chitosan has a strong affinity for dyes, and is adhesive to many nonmetallic substances, including glass, rubber, and an extraordinary number of synthetic filaments and fiber materials. The presence of charged amino groups regularly spaced along a polymer chain having the same spacing relations as cellulose enables chitosan to bind to cellulose with ionic as well as hydrogen bonds, thus creating a stronger affinity than exists between cellulose-cellulose pairs. This strong binding affinity supports a number of potential applications in adhesives, coatings, sizes, binders, etc., for cotton, wood, and paper, and regenerated forms such as cellophane and rayon (see 2.3, Candidate Applications).

A final category of chitosan's properties and capabilities that can be exploited in applications to be discussed later is the formation of insoluble complexes with suitable electronegative polymers. Water- or alkali-soluble cationic polyampholytes containing amino-, imino-, or guanido- groups, and having isoelectric points lying in the alkaline range, can be coprecipitated with sodium alginate (or other water-soluble alginates) to form insoluble complexes that yield films with interesting properties. This occurs in an acidic bath, where the polybase acquires positive charges to become polycationic and thus able to react with the negatively charged alginic acid.[4,6] These coprecipitated films are much less subject to swelling and exhibit increased strength over pure alginate films, and can be modified to adjust these and other characteristics. Hydroxyethyl chitosan and carboxymethyl chitosan are among the macromolecular bases or polyampholytes that can be used in this application, since they have solubility and isoelectric points in the alkaline range such that intimate mixing with alginate can be achieved before acidifying the solution to induce protonation of the chitosan and formation of the insoluble complex.

The carboxyl groups of alginic acid may be wholly or partly saturated by the polybase, thus controlling the properties of the complex. Saturation reduces swelling and augments mechanical strength. The remaining free carboxyl groups of an unsaturated complex can be wholly or partly replaced by other ions (ammonium, potassium, sodium, magnesium, and particularly *calcium*), by submitting the complex, after acid precipitation, to a solution of calcium salt (acetate or hydroxide). Negligible displacement of this calcium will subsequently occur in the presence of sodium and the swelling tendency in NaCl or H_2O is reduced 90%.[4]

As a cationic polyelectrolyte, chitosan readily forms insoluble complexes with anionic polyelectrolytes such as carboxymethyl cellulose,[39] lignin sulfonates, natural tannins, and certain coloring matters. Many of these complexes have film-forming properties or make stable gels.[6]

A similar ionic reaction takes place between heparin (a highly sulfated mucopolysaccharide) and chitosan in dilute acetic acid solutions to form a water-insoluble complex.[34] This polyelectrolyte complex is soluble in formic acid or in acetone, potassium bromide, and water. It can be esterified with various organic acids to produce derivatives that are stable in formic acid and/or dimethyl sulfoxide (DMSO).

2.2.3.2 Other Chitin Derivatives Several ethers have been obtained by reacting appropriate reagents with alkali chitin swollen further by DMSO. Hydroxyethyl, carboxymethyl, and ethyl chitins are all known to be enzymatically degradable by lysozyme[2,43,44] and therefore to be solubilized if bathed by human body tissue fluids. In addition to the ethers, there is a small number of esters, but little, if anything, else has been reported.

Carboxymethyl Chitin Poly[N-acetyl-6-0-(carboxymethyl)-D-glucosamine] can be prepared by swelling chitin in DMSO and treating the swollen mixture successively with 2-propanol, NaOH, chloroacetic acid, then treating the solid residue with methanol and neutralizing with acid.[2] The resulting carboxymethyl chitin is soluble in water at 5%, and is degradable by lysozyme.

The analogous derivative can be obtained from chitosan, making it also soluble in the alkaline range.

Hydroxyethyl Chitin Poly[N-acetyl-6-0-(2'-hydroxyethyl)-D-glucosamine] can be prepared by reacting ethylene oxide in an autoclave with chitin swollen in alkali and then DMSO (for example, see reference 2). Hydroxyethyl chitin is water soluble at 5% and is degradable by lysozyme.

Ethyl Chitin Poly[N-acetyl-6-0-(ethyl)-D-glucosamine] can be made by a procedure similar to that for hydroxyethyl chitin except for the substitution of ethyl chloride in the place of ethylene oxide and an increase in the reaction time or temperature. Control of reaction conditions gives control of the degree of substitution obtained, which, in turn, determines the solubility. The product is water soluble if the degree of substitution[i] is not greater than about 1, and is soluble in organics such as benzene, xylene, toluene, methyl ethyl ketone, chloroform, and alcohols if the degree of substitution is greater than about 1.

The viscous solutions obtainable with ethyl chitin have yielded membranes with good mechanical properties (5.5–7.3 kg/mm^2 tensile strength and 5–23% elongation). Ethyl chitin is degradable by lysozyme but, unlike ethyl cellulose, does not melt.

Glycol or Glycerol Ethers of chitin or chitosan have been described, and analogs with other polyhydric alcohols should be feasible.[9] Ethylene glycol chitin is degradable by lysozyme.

Glycol Chitosan Glycol chitin, as prepared by Senzyu and Okimatsu,[7] is mono (hydroxyethyl) chitin. Since only the primary hydroxyl of chitin is selectively glycolated, it should be possible to glycolate chitosan, also.

Cyanoethylated Chitosan (Treatment for electrical insulating paper.) Russian patent.[16]

Chitin Acetate Both homogeneous and heterogeneous acetylation can be obtained.

Chitin or Chitosan Nitrates Substantial nitration of chitin has been obtained in concentrated acid, or in fuming nitric acid, which induces considerable chain length degradation.[9] Chitosan dissolves in absolute nitric acid to give the nitric acid salt of chitosan nitrate ester, approximately 85% esterified. Suspensions of chitosan in glacial acetic acid containing perchloric or nitric acid yield the corresponding amine salts. The perchlorate salt of chitosan nitrate has also been prepared, but is spontaneously, and possibly explosively, unstable.

Chitin and Chitosan Sulfates Chitosan can be sulfated with chlorosulfonic acid in pyridine to yield an amorphous sodium salt containing both N- and O-sulfate groups and possessing blood anticoagulant activity.[11] Various modifications including prior carboxylation or the conversion of some of the sugar units to uronic acid units, have been investigated in attempts to model artificial anticoagulants after the natural anticoagulant heparin.

Chitin can also be sulfated with chlorosulfonic acid, yielding the chitin disulfate half-ester, which is water soluble and has about one quarter the anticoagulant activity of heparin.

2.3 Suggested Uses for Chitin or its Derivatives

A survey of suggestions for application of these compounds reveals that chitosan has received more attention than chitin or its other derivatives, and that chitosan's uses are largely determined by its high binding capacity for other substances. Its affinity for cellulose products is further enhanced by the structural similarities of the two polymers, providing regularly spaced matching of repeating ionic, as well as hydrogen, binding sites.

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[i] That is, the average number of ethyl groups per sugar residue.

As a result of this peculiar matching and high bonding affinity for cellulose, many functions dependent on or enhanced by this property have been tested or proposed. They include:

(a) *Adhesives for cellulosics*, e.g., various combinations of wood, paper, cotton, or regenerated cellulose (including cellophane and rayon). Such applications encompass joining or laminating any combinations of these cellulose-related substances, and benefit from water- and- oil- and heat-resistant bonds that are commonly stronger than the substrates.

(b) *Binders and strength additives for cellulosics*, e.g., for paper pulp or reconstituted tobacco sheet,[j] and may logically be extended to analogous concepts, as yet untested, such as reconstituted cork products. The inclusion of 1–2% chitosan in paper or nonwoven fabrics imparts increased interfiber bonding and can replace some of the beating process or chemical pulp that is alternatively employed for this purpose. The resultant papers or mats have increased dry and wet burst and tensile strengths and improved drainage, with retention of clay or other fine particle fillers. Dry strength improvement is also claimed for the addition to paper pulp of a 2-acrylamido-2-methylpropane sulfonic acid graft copolymer with chitosan.[17]

(c) *Sizings or coatings for cellulosics*, e.g., on paper, natural cellulose fibers (cotton, linen, etc.) and on regenerated cellulose (cellophane, rayon, meat casings, etc.). Chitosan has been considered as a potential sizing or surface treatment for paper to impart characteristics needed for graphic processes, such as moisture- and pick-resistance for lithography and offset printing, or modification of electrical characteristics, as for xerographic processes.[k]

Various methods have been demonstrated for the application of chitin or derivatives as sizings on cellulose textiles and other fibers for control of moisture and soil resistance and to impart desirable laundering, finishing, and shape retention characteristics. These include chitosan solutions in acetic acid, chitin xanthates, chitosan xanthates, and xanthates of sulfonated derivatives.[20,35,36,37,40,41]

Low viscosity chitosan, 3–4% in acetic acid, adheres very strongly to rayon and can produce a water-resistant surface on cellophane (probably with reduced gas permeability, especially to CO_2). It greatly improves the dyeability of these synthetics and could be expected to reduce or eliminate the "crocking" or dye rub-off problems in cellulosic meat casings.

(d) *Constituent or copolymer in cellulosics*, e.g., in regenerated cellulosic fibers and films. Inclusion of 1–10% by weight of chitosan in cellulose regenerated from a mixed xanthate markedly improves the dyeing characteristics.[17] Chitin can also be used in mixed xanthates with cellulose to produce fine fibers with ramie-like quality and with improved dyeing characteristics.[18]

(e) *Adhesives and sizings for nonmetallic noncellulosics*. Chitosan can also perform similar adhesive and sizing functions with noncellulosic materials, due to its affinity for a great variety of nonmetals, especially glass, rubber, and many synthetic fibers and plastics. As a permanent all-purpose sizing for glass fibers, it could act as a lubricant, to reduce abrasion and breaking during handling, or as a dye binding agent, or as a coupling layer to bond plastic matrix to the fiber in FGP laminates.

Because chitosan is compatible with gelatin in solution, it can be included in photographic film emulsions to facilitate binding of dyes used in color processes. The gelatin is also mechanically strengthened by its presence.[19]

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[j] Pyrolysis of chitin yields a pleasing aroma not incompatible with tobacco smoke. The condensate is reported as very small, with little or no evidence of carcinogenic components.

[k] Cyanoethylated chitosan has also been discussed as a paper treatment for producing electrical insulating papers.[16] Insulating paper development is currently stimulated by the prospect of a ban on polychlorinated biphenyls in the manufacture of high voltage capacitors.

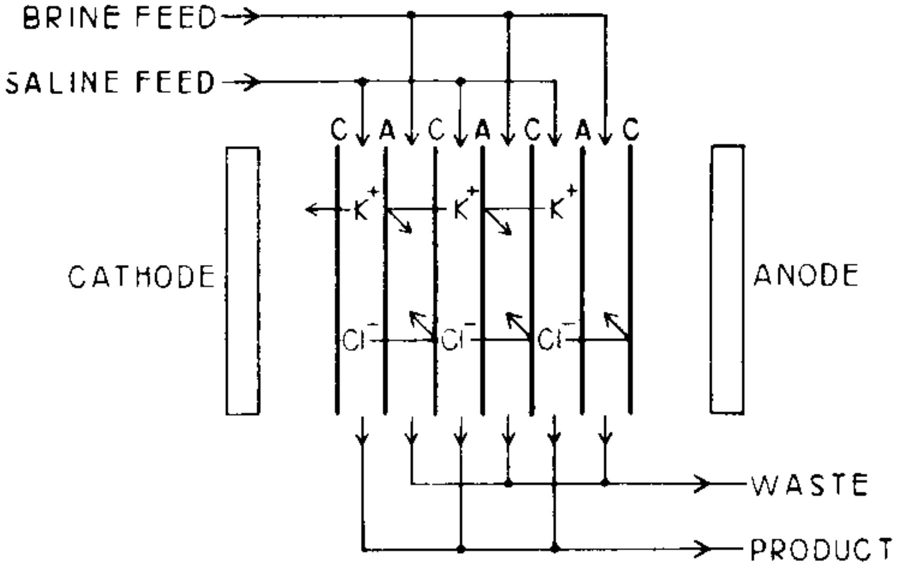
Glass, cellulose acetate, silk, wool, or synthetic polymer fibers (e.g. Orlon, Creslan, Acrilan, Dynel, Soren, Dacron, Nylon), when treated with a water solution of chitosan and a Werner-type reactive chromium complex such as p-aminobenzoate chromic chloride, acquire a coating that can be dyed much more easily. The treatment is dried and fixed in place by heating, during which process the chromium compound polymerizes and binds mutually with the chitosan and the fiber substrate.[35]

A possibly analogous application employs chitosan to aid in binding a silicone to cotton fabric to obtain a permanent, wash-fast, water-repellancy.[20]

Sulfated chitin or chitosan xanthates also can be deposited onto noncellulosic materials such as glass, ceramics, metals, wool, silk, and other proteins, polyesters, polystyrene, polypropylene, polythylene, polyurethane, polyamides, etc., where they impart antisoiling and/or antistatic characteristics.[36]

(f) *Films and fibers*. While pure chitin or chitosan films or fibers are obtainable from xanthates or, in the case of chitosan, from casts or extrusions from acid solutions, only the most rudimentary studies have been made of their properties and few serious suggestions for their use have been advanced. While awaiting further elucidation of pure film and fiber characteristics, it may be kept in mind that the films are transparent and, for chitosan, easy to dye, relatively impervious to carbon dioxide, and appear to have movable chain spacings that can accommodate other molecules (e.g., plasticizers?)

One possible application that would take advantage of both chitosan's film-forming property and its relatively high charge density would be in ion exchange membranes. Currently, the largest use for such membranes is in electrodialysis apparatus, for desalinization, as illustrated below:



Up to 600 membranes between one set of electrodes

The basic principle of electrodialysis is that positively charged ions will pass through a negatively charged (cationic) membrane very well, but the electrical repulsion from like charges excludes them from entering and passing through a positively charged (anionic) membrane. Conversely, negatively charged ions will pass a positively charged membrane but not a negatively charged membrane. In the diagram above, salt water enters the top of the membrane stack and lateral migration of the ions is induced by the presence of an electric field. Because of the presence of different membranes of alternating charge, ions are depleted and enriched in alternating compartments. For desalinization operations, the "low salt" compartments yield product water. A number of other applications for ion exchange membranes also exist.[24]

Experimental interest in wound healing applications (see below) includes the possible use of chitinous films as protective wound coverings or chitinous fibers as suture materials. However, the special combination of requirements for an ideal suture are sufficiently challenging that it may prove advantageous to consider combinations and modifications that would enable one to select or manipulate the properties of the fiber. Thus, as in meat casings, variations on or analogs of chitosan derivative-alginate materials may provide such a means for manipulating properties. As described in Section 2.3.3, carboxymethyl chitosan or other suitable derivatives can be complexed to alginic acid to yield insoluble, film-forming materials with characteristics that are useful in meat casings. They show improvement over pure alginate casings since they are much less subject to swelling, exhibit increased strength and adherance to meat, and can be modified to adjust their physical and chemical behavior. However, absorbability in a physiological environment has not been tested.

(g) *Collection and separation of ions, molecular species, and suspended particles.* The selective binding characteristics of chitosan can be exploited in numerous ways. When packed into cartridges or columns, its remarkable chelating ability will very efficiently remove certain metals from liquids passed through the column. Since it will not bind to and is relatively unaffected by the presence of groups IA and IIA alkali and alkaline earth metals, their presence has no appreciable effect on the collection of transition metals. In this regard, it is better than synthetically-substituted celluloses or polyaminostyrene. With these advantages, chitosan is suited to the collection of zinc, cadmium, lead, silver, and copper from sea water,[21] and for the quantitative removal and determination of very dilute concentrations of certain other metals including mercury, vanadium, and molybdenum. The collector can be regenerated with a small volume of sulfuric acid, yielding a concentrated solution of the collected metals. It may also be anticipated that chitosan could find use in the removal of mercury from the waste of chloralkali plants, or electrolytic cell brines, the removal of chromium from the rinse water wastes of electroplating processes, or the removal of cerium, zirconium, and niobium radioisotopes from nuclear fuel solutions so that the fission indicator, cesium-137, can then be determined without interference.

Since chitosan binds selected metal ions so well in the presence of brines, it can, if pretreated with such metal ions, subsequently collect anions or complexing agents such as cyanide, phosphates, or amino acids from waters or brines without loss of the chelated metal. Thus, traces of cyanide in concentrated ammonium sulphate solutions discharged from acrylonitrile plants can be separated for recovery of the brine.

Metal chelates on a chitin matrix are also useful for the insolubilization of soluble enzymes, such as glucose oxidase,[45] to facilitate subsequent reactions with specific enzyme substrates, as in the automatic determination of glucose in hospital laboratory diagnostic instruments. Various other enzymes can also be immobilized on chitin or chitosan supports, by various means, including linkage by glutaraldehyde.

Lysozyme-like enzymes, for which chitin is a substrate, as well as other substances such as wheat germ agglutinin that binds specifically to N-acetyl glucosamine, will of course bind specifically, and can therefore be purified and collected on chitin adsorbants.[15] Chitin is also useful for the chromatographic separation of a number of other biochemicals, including nucleic acid constituents, that are of interest in clinical or research laboratories.

Because of its great density of free amino groups, chitosan may have appreciable utility in general laboratory chromatography. Since it can be dissolved in acidified waters and then precipitated by alkalis, its flocculating action may be added to its ionic binding characteristics so as to affect bulk removal from liquids of solubles such as thyroglobulin, which it is capable of binding. In other cases, the generation of a gelatinous, flocculant precipitate can trap and facilitate the removal of finely divided suspended solids occurring in various products to be clarified, or which must be removed from liquids for reclamation or disposal of either the liquid or solid phase. Generally, it has been found that chitosan gives comparable or better results than synthetic polyelectrolytes in the treatment of waste liquids and would be the material of choice if its cost were sufficiently low. In special cases its technical superiority and the value of the product that can be recovered can offset the cost. As a tentative example, utilization of chitosan in the reclamation of fine paper pulp fibers might have the double advantage of retrieving a valuable paper component, as well as serving a later, strength-additive function when the chitosan/fiber mass is added back into the paper process.

(h) *Pharmaceuticals*. Chitin, when free of its naturally-associated proteins, is nonantigenic in humans,[46] and may be inserted under the skin, in mucous-wetted cavities or in contact with body fluids, without harm. In such a location, it will be slowly attacked by tissue enzymes and absorbed. Since it has been found to accelerate the natural fusion and healing of incisions and other wounds, an interesting spectrum of surgical applications is suggested and has been under study for several years.[l] These studies include the use of chitin powders and ointments for wound treatment, chitin (or chitin-treated) covers as temporary wound prostheses, chitin or chitin coatings for surgical sutures, and for other surgical adjuncts. So far, these efforts have resulted in five U.S. patents[m] (plus foreign coverage) and at least five NDA's (investigational new drug applications) to the Food and Drug Administration (FDA), and development is actively continuing.

The phenomenon of slow absorption has also prompted consideration of chitin or degradable derivatives as materials for controlling the slow release of drugs within the body or in special external locations such as the eye, whose bathing fluids are rich in lysozyme. As an example, the drug pilocarpine has been cast in carboxymethyl chitin matrix and chronically inserted under the eye lid, in which position it is slowly dissolved by enzymes in the tears, releasing the drug over an extended period of time. Various other chitinous matrices, drug combinations, and body locations are also feasible.[2]

Glucosamine itself, which is obtained from the complete hydrolysis of chitin, has also been found selectively toxic to tumors and cultured tumor cells[47] and might eventually be useful in the clinical management of cancer. It has also been in use as an adjunct to antibiotics but the trend of such use is presently sharply down because of FDA's general disapproval of drugs in new combinations until NDA's are obtained for the combination as well.

2.4 Production Chemistry for Chitin and Chitosan

A variety of procedures has been employed for the extraction of chitin from crustacean shells and for making the deacetylated derivative, chitosan. Among these methods, there is a significant difference between best laboratory methods and satisfactory methods that may be best for a manufacturing scale, where costs are important. In general, extraction of chitin entails steps to demineralize and deproteinize. Laboratory procedures generally include treatments in organic solvents to remove pigments, etc. On a production scale, demineralization and deproteinization have been accomplished by successive treatments in dilute mineral

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[l] An initial publication, Prudden et al, *Am. J. Surgery 119* (1970) 590, has not been followed by further publications, but several subsequent patents are available for reference.

[m] These patents are currently free of encumbrance, and available for license or other possible arrangements, and include US 3,632,754; 3,903,268; 3,911,116; 3,914,413; and 3,624,201.

acids and dilute alkali, in either order. The resulting chitin can then be deacetylated by cooking, at atmospheric pressure, in an excess of 40–50% caustic soda.

All of the acid and alkali treatments cited cause some undesired degradation of the product. Acids used for decalcifying also remove a few acetyl groups; and alkalis, especially at elevated temperatures, cause a certain amount of depolymerization. Thus, if favored for commercial use because of their cost advantage, such operations must be judiciously controlled.

A typical commercial process sequence for extracting chitin and by-products from crustacean shell waste is illustrated on page 14.

Immediately after grinding, and before any chemical processing, bits of flesh and other soft tissue are separated from the shell and recovered from a water slurry. *This material is a high grade food stock suitable for fish, poultry, and other animals, and is the principal by-product of value obtained in the chitin extraction process. Because of its value, it is feasible for most shell processors to carry out only the steps leading to this dried or frozen feed supplement and a clean shell residual.* The latter is more negotiable waste than raw shell, and may, if dried, have at least a break-even value in resale to a chemical processor. (See section 3.1.3).

Further processing consists of removal of the calcareous mineral constituents and the protein that is an integral part of the chitinous shell. Minerals (largely $CaCO_3$) can be removed in a weak acid solution that may be recycled until it is nearly exhausted. Protein can be removed by a 1% alkali solution in about 24 hours at room temperature in a stirred vat, or in ½ to 1 hour if steam heated.

Chitin produced by this method may then be converted to chitosan or other derivatives. However, if chitin is not a desired product, there is no necessity of isolating it as an intermediate simply for chitosan conversion. Deacetylation and deproteinization could be accomplished in a single step, by cooking in strong caustic immediately after demineralization.

The conventional conversion to chitosan is accomplished by prolonged heating in 40–50% caustic soda. Such a treatment, in the presence of oxygen and water, may give rise to considerable polymer chain breakage, yielding a mixture of chain lengths in the products. For laboratory quantities, it is advantageous to make the alkali solution in ethylene glycol or alcohol-ethylene glycol, or to suspend a paste of chitin/50% aqueous NaOH in paraffin oil, or to substitute 50% potassium hydroxide in diethylene glycol.[9] Such measures minimize the water present, hindering undesired hydrolysis of the polymer backbone.

Other laboratory variations in processing have been applied to chitin extraction, substituting a powerful calcium chelator (EDTA)[n] for acid in the demineralization step, or employing crude enzyme preparations for deproteinization.[9] As with the nonaqueous deacetylation procedures, these other variations have been adopted because they are gentler and may have fewer unwanted side effects.

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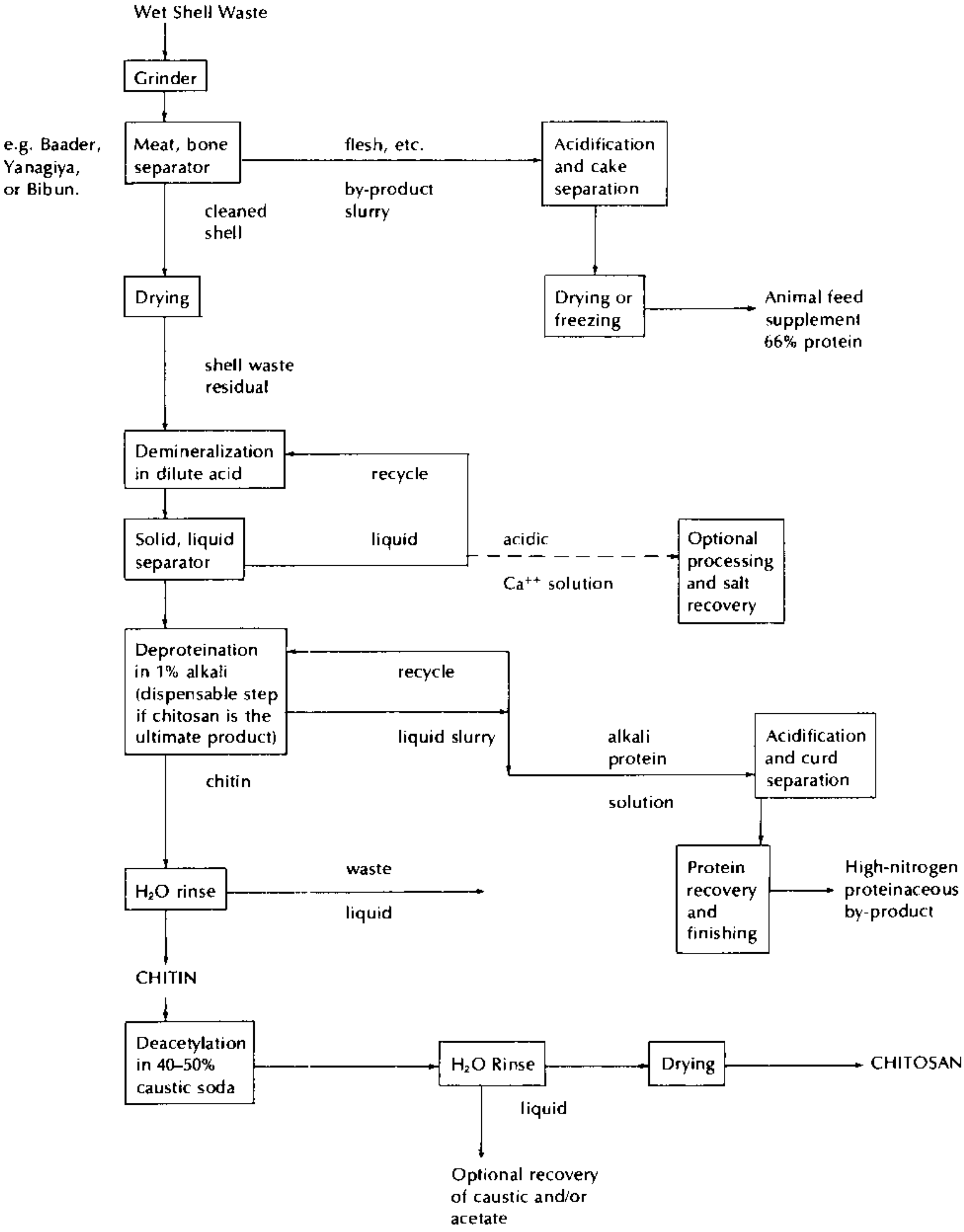
[n] Ethylene diamine tetra-acetic acid


Wet Shell Waste
Grinder
e.g. Baader, Yanagiya, or Bibun.
Meat, bone separator
flesh, etc.
by-product slurry
Acidification and cake separation
cleaned shell
Drying
Drying or freezing
Animal feed supplement 66% protein
shell waste residual
Demineralization in dilute acid
recycle
Solid, liquid separator
liquid
acidic
Ca++ solution
Optional processing and salt recovery
Deproteination in 1% alkali (dispensable step if chitosan is the ultimate product)
recycle
liquid slurry
alkali protein
solution
Acidification and curd separation
chitin
H2O rinse
waste
liquid
Protein recovery and finishing
High-nitrogen proteinaceous by-product
CHITIN
Deacetylation in 40–50% caustic soda
H2O Rinse
Drying
CHITOSAN
liquid
Optional recovery of caustic and/or acetate

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3 REALITIES OF SUPPLY

In this chapter, we seek to predict the amount of chitin or chitin derivatives that is likely to be produced in the U.S. if the price for these materials achieves various levels. In economists' parlance, we wish to estimate the long-run supply function.

Unfortunately, the techniques that are most often used by economists to estimate supply functions depend on observing the results of past market action — prices and quantities sold — and from these inferring the response of production levels to different market prices. In the present case, there is no history of appreciable past sales to observe.[a] The approach we must take, therefore, instead of analyzing the results of market action, is to focus in detail on the process of production and associated costs. From the operating costs and capital requirements, we infer the minimum product prices that would be necessary to provide a return on investment sufficient to encourage investments in the amounts required for various levels of production.

To be more explicit, we assume that the minimum required price of the product chitosan on a per unit volume basis can be expressed as:

> (Net costs of collection of shell wastes) + (Costs of other processing steps and associated business costs) − (Credit for sale of by-product protein) + (Minimum required return on investment) = (Minimum anticipated product price required for investment)

With the exception of the minimum required return on investment, each of the variables in the above equation is a function of the volume and location of production and must be evaluated on those bases.

It should be emphasized that the estimates of *minimum anticipated product price required for investment* that will be presented in this section should not simply be interpreted as estimates of the ultimate *market* price that chitosan will command. However, if the market price expected on the basis of the analysis in Section 4 (Demand Analysis) is above the minimum required price for a given volume of production, rational investors will be inclined to risk the capital needed to institute that volume of production. Conversely, if the expected market price appears to be below the minimum required price for a given volume of production, rational investors will tend not to make the required investment.

To make our analysis manageable, we have made a number of simplifying assumptions about costs, waste composition, and other aspects of the probable production scheme. It is our intention to be as explicit as possible in stating these assumptions and in showing how they have been used, so that as more precise information becomes available the reader may modify or adapt the analysis to actual prevailing conditions.

We conclude:

- Production of by-product protein makes an important contribution to the economic viability of chitosan production. Under an optimistic set of assumptions about protein

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[a] As of this writing there are two plants in the U.S. that are producing chitin from commercial waste. One (Food Chemical Research Laboratories, Seattle, Washington), with a designed capacity of about 75,000 pounds per year, began operations in the early 1970's under contract with the U.S. Office of Sea Grant to produce small quantities of chitin and chitosan for research and development. More recently, a plant with a capacity of about 500,000 pounds per year has been opened by Marine Commodities International (MCI) in Brownsville, Texas. There is no evidence to date that major volume sales have occurred. Hercules Inc., which has an exclusive contract to market the MCI product, offers small quantities of chitosan at a price of $5–7 per pound.

price, the initial mechanical separation of protein from shell can yield a sufficient return to justify investment without any contribution of revenue from further process steps. Under a more pessimistic set of assumptions, the sale of protein is nevertheless important in reducing the minimum required price of chitosan.

- The most viable industrial organizational schema is a two-step production sequence:
  - Local production of dried protein and shell waste residual by large or centrally located shellfish processors, drawing shell waste from their own operations and (possibly) from other shellfish processors within a 50 mile radius.
  - Shipment of the dried shell waste residual to a regional or national chemical industry facility for production of chitosan.
- Chitosan production of between 1 and 4 million pounds is likely to be feasible from shellfish wastes with a minimum anticipated price of chitosan between $1.00 and $2.50 per pound.
- If the demand for chitosan exceeds the 1 to 4 million pound range and is capable of supporting higher chitosan prices, sources of chitin other than shellfish waste may be brought into production. The most promising of these "other" sources are fungal waste by-products from citric acid and other industrial fermentations.

3.1 Chitin from Shrimp and Crab Waste in the U.S.

This section is divided into five parts. First (Section 3.1.1.), we specify the form of industrial organization — the types of business-business linkages and the division of production tasks — that is most likely to lead to a viable industry. This organizational schema then forms the basis for the ultimate assessments of cost.

The second part (Section 3.1.2) assembles available data on the amounts of different kinds of shellfish waste likely to be available for production of chitosan and protein in different areas. *Areas* are defined as 50 mile radius circles drawn to include the maximum possible numbers of shellfish processing plants.

The third part (Section 3.1.3) introduces information on the probable composition of wastes from different sources. Together with data on waste availability from the second part, this forms the basis for estimates of the total quantities of chitin potentially producible from the waste in different areas.

Following this, the fourth part (Section 3.1.4) analyzes the economics of production from the standpoint of a local shellfish processor considering manufacture of protein and shell waste residual. The question addressed is "What price of shell waste residual (based on chitin content) is necessary to induce production of various quantities in different areas?"

Finally, given this assessment of the supply function for shell waste residual, the fifth part (Section 3.1.5) addresses the question, "What price of chitosan product is necessary to allow a chitosan producer to pay the prices necessary for the production of various quantities of shell waste residual in different areas?"

3.1.1 Industrial Organization for Utilization of Shellfish Wastes

Commercial production of chitosan and protein from shellfish wastes requires successful performance of the following set of tasks: (1) procuring shellfish wastes, (2) manufacturing protein and chitin products, (3) conducting the research and development necessary for the establishment of viable markets, and (4) entering and selling to those markets. Different tasks within that set involve considerably different industrial capabilities, and the history of previous attempts at chitin production has generally been discouraging, partly because the performance of one or more of the tasks has been weak or absent.

To envision how the full set of tasks could be brought into being, it will be helpful to describe the characteristics and needs of four kinds of companies that have shown interest or involvement with chitin production in the past.

> *SHELLFISH PROCESSORS.*[b] These companies possess the shellfish waste, and any practical schema to utilize such material must have sufficient attractiveness to this group to enlist the companies' active participation. In general there is pressure from community and environmental authorities on shellfish processors to find alternatives to disposal of shellfish wastes in landfills or as liquid effluent. Other use for waste in some areas is in the production of shrimp and crab meal — which are, however, very low-value products. The chitin business offers these firms an opportunity both to help eliminate a waste disposal problem and to upgrade the value of their output. On the other hand, companies in this category have repeatedly stressed to us that they are in the food business, not the chemical business, and they would have to acquire a whole new set of skills and modify their overall corporate strategy in order to undertake the production and marketing of chitin or chitin derivatives.
>
> *SMALL ENTREPRENEURIAL CHITIN/CHITOSAN SPECIALITY MANUFACTURER.*[c] Formed by a few motivated individuals with a limited amount of venture capital, these companies have tended to initiate production largely on hopes that forces beyond their control would operate in their favor. Because they have not had control of large sources of raw material, they have been subject to fluctuations in the willingness of shellfish processors to provide them with waste at affordable prices. Because they have found it difficult to sustain long-term technical efforts in product development, they have had to rely on others (potential consumers and government agencies) to make appropriate investments in developing chitin/chitosan technology. Because they are small, new companies without the credibility and customer connections of an established big-name firm, they have had to rely largely on the product's ability to sell itself. These problems are not an absolute bar to success, but there is clearly room for such companies to improve their probability of survival by entering into agreements with other firms to bring more of the determinants of success under control.
>
> *MAJOR DIVERSIFIED CHEMICAL COMPANIES.*[d] Firms of this category have capital, technical expertise, and market connections that may enable them to exploit profitably the commercial potential of new chemical products. However, innovations must make their way through corporate bureaucratic structures and occasionally a particular new application may tend to compete in unwanted ways with the firm's established products.
>
> *MAJOR PROSPECTIVE CONSUMING COMPANIES.*[e] Before potential consuming companies invest appreciable funds in research to investigate the feasibility of using chitin/chitosan products in their operations, quite understandably they

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[b] Among the sponsors of this project, for example, is a major West Coast crab and shrimp processor, Castle & Cooke. Also in this category may be placed the few existing crab-meal and shrimp-meal firms.

[c] At present, Marine Commodities International and Food Chemical Research Laboratories are the two companies in this category.

[d] Union Carbide, a sponsor of this project, is in this class. Additionally, Hercules (which currently has an exclusive contract to distribute products from MCI, and an option to buy MCI) is in this category, and in the past other major chemical firms such as DuPont have participated in chitin development.

[e] Kimberly Clark, a maker of paper products, at one time showed an active interest in chitin. Additionally, Weyerhaeuser held an option at one time to buy the FCRL operation in Seattle (which was allowed to lapse in mid-1975) and Crown Zellerbach reportedly sought to purchase a large quantity of chitosan a few years ago.

wish to be assured of a significant continuous supply of these materials at reasonable cost. Before entering into commitments for major purchases, of course, experiments must demonstrate the cost-effectiveness of the chitin/chitosan products, as compared with available alternatives, for the uses the companies contemplate.

These are the types of companies potentially involved in shell waste utilization. Three different arrangements of roles and relationships are shown in Figure 3.1.

FIGURE 3.1

Type of Firm	*A* *(FCRL Model)*	*B* *(MCI Hercules Model)*	C
Shellfish processors (Dispersed in many areas of the country)	Provide wet waste for trucking to chitin/chitosan production plant. (Local)	Provide wet waste for trucking to chitin/chitosan production plant. (Local)	Large central processors separate by-product protein from wet waste.* Dry both the protein and the chitin containing shell waste residual. The protein is sold for animal feed and the shell waste residual is sold to a chitin/chitosan producer. (Local)
Small, entrepreneurial specialty firms	Perform all processing steps through chitosan and attempt to induce prospective consumers to perform R & D to develop applications. Also sell protein by-product. (For nation-wide production, many plants required in dispersed locations.)	Perform all processing steps through chitosan, but market chitosan through a major diversified chemical company. Sell protein by-product. (For nationwide production, many plants required in dispersed locations.)	Provide technical assistance for shellfish processors to set up wet waste collection, protein separation and drying systems. Purchase the shell waste residual from the processors, and possibly act as marketing agent for their protein.
Major diversified chemical companies	No role	R & D on applications necessary to develop markets. Sales of chitosan to those markets. Technical assistance to both consumers and to the chitosan producer.	Manufacture chitosan from the shell waste residual at a large national facility.** R & D on applications necessary to develop markets. Sales of chitosan to those markets. Technical assistance to customers.
Prospective consumer companies	Together with government sponsored academic researchers, undertake R & D. Eventually, purchase product.	Purchase product.	Purchase product.

*The wet waste can be the wastes produced by the shellfish processor's own operations and (optionally) additional wet waste trucked in from other shellfish processors in the same area.

**The placement of this manufacturing step could conceivably be either where we show it here, with the small entrepreneurial firm, or with the major diversified chemical company. The latter alternative would make the small entrepreneurial firm basically an organizer and provider of technical and marketing services.

Historically, the major impetus for the start of chitin/chitosan production has come from small entrepreneurial specialty firms, which have borne the principal responsibility for developing all business functions through processing and marketing in order to get the business start-ed. This places an enormous burden on a small firm — developing and operating all the manufacturing steps, stimulating others to investigate and develop applications, and then undertaking all the necessary marketing. Food Chemical and Research Laboratories, Inc. (FCRL), in Seattle, currently represents this type of venture (see model A, Fig. 3.1).

Marine Commodities International, Inc., in Brownsville, Texas, also began in this way but late in 1975 arranged with Hercules, Inc., to shift all marketing and much research and development responsibility to them. (See model B, Fig. 3.1). Recently, however, they have encountered unanticipated problems with raw material supply.

Arrangement C of Figure 3.1, which shifts most of the processing steps away from the small entrepreneurial firm, has not yet been tried but is under consideration. Compared to the B model, C requires the extra steps of drying a preprocessed shell waste residual and transporting it to a national (or regional) chitin/chitosan production facility. On the other hand, the C model has the following advantages:

- Shellfish processors under this schema have greater incentive to participate — they get a waste disposal system that can be operated at their convenience and under their immediate supervision to produce a proteinaceous, food-related product for a market they understand.
- The large national (or regional) facility for manufacturing chitin/chitosan from shell waste residual can take advantage of economies of scale and location[f] and perform the demineralization and deacetylation steps at lower unit cost.
- The small entrepreneurial firm can concentrate its efforts on what it does best — stimulating and organizing the technological change.

For these reasons, we believe that model C represents the arrangement of business-business relationships most likely to succeed. Our analysis of economic costs in the following sections proceeds on that basis.

3.1.2 Availability of Different Types of Shell Waste in Different Areas

Previous estimates of the quantity of chitin potentially producible from shell waste in the U.S. have generally ranged from the neighborhood of 25 million to as much as 100 million pounds per year. For the most part, these figures seem to have been based on the gross quantities of different kinds of shellfish caught and on apparently generous assumptions about both the volume of the waste practically available to a chitin plant and the likely ultimate percentage yield of dry chitin from the waste.

3.1.2.1 Inventory of Shellfish Processing by State The starting point for our analysis is not overall landings, but a detailed inventory of the quantities of individual kinds of shellfish products processed into various kinds of ultimate products, distributed geographically among sites where processing is performed. It is important at the outset to exclude as practical chitin sources those processed products that are marketed in the shell. (It is not likely to be economically feasible to recover shell from the ultimate consumers of shellfish.) Tables 3.1a through 3.1f (see Appendix) summarize National Marine Fisheries Service data for 1972 on both the live weight of different shellfish landed and the product (marketed) weight of various processed products for different states.[1] In these tables, the products whose processing results in chitin-containing waste are shown in italics, and those that do not are shown in bold face.

There must be two qualifications attached to this presentation:

First, for shrimp marketed in the shell (e.g., *raw headless* shrimp), there is in general a possibility of recovering chitin and protein from the waste heads. However, we shall estimate

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[f] One type of economy of location is created by the substantial variability in costs of hydrochloric acid for demineralization. Acid is about 50% more expensive on the West Coast than it is in the Southeast. As will be seen later, this difference in acid cost strongly militates against chitosan production in the West — however, shipment of shell waste residual from the West to the Southeast may not be prohibitively expensive.

shrimp head waste separately below, as this is frequently associated with sites of landing, which are in some cases different from the sites of processing.

Second, the NMFS data are necessarily based on information reported to them by individual processors. We have been cautioned by persons knowledgeable in the field that some processors tend to understate their actual production volumes in order to avoid possible complications with the Internal Revenue Service.

3.1.2.2 Geographic Definition of Potential Shell Waste Processing Sites After tabulating, by state, output of products whose processing yields chitinous waste, our next steps are to: (1) define the size of the geographic area from which a waste processor is likely to be able to draw his raw material, and (2) decide approximately the most favorable locations for shell waste processing within individual states. Wet shell waste is a very low density material[g] with a substantial content of water[h] and a relatively modest content of chitin.[i] These characteristics make the transportation of wet waste for long distances a considerable expense.[j] Because of this, we have chosen to make assumption #1.

> *Assumption #1: Shell waste processing facilities will, in general, need to draw the great bulk of their raw material from within a 50 mile radius.*

From a National Marine Fisheries Service[2] listing of names, addresses, and major product types of individual shellfish processors across the U.S., we have constructed a series of maps (see Appendix) showing the distribution of shellfish processors in different states and groups of states. Utilizing Assumption #1, there are 50 mile radius circles on each map drawn in such a way as to include the maximum numbers of processing plants. In further analysis we shall consider each of these designated circles to be the effective collecting area for a plant processing shell wastes.

3.1.2.3 Live Weight of Shrimp and Crab Processed in Different Areas Authoritative estimates of the quantity of shellfish waste available within the 50 mile circles would depend on detailed production data by plant or by other subdivisions of the individual states. Since this information is not published, Assumption #2 is needed in order to derive some approximate figures.

> *Assumption #2: The fraction of each state's total shrimp shell and crab waste that is available in each area is proportional to the fraction of each state's shrimp and crab processing plants that are contained in each area.*

For example, if a state has a total of 10 shrimp processing plants, 6 of which are located within a particular 50-mile radius area, we assume that approximately 60% of that state's shrimp shell waste will be located within that area.

One other transformation of the data in Tables 3.1a–f will be made prior to calculating actual quantities of wet waste available. Table 3.2 shows the relationships between live weight of

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[g] Shrimp shell waste weighs only about 13 lbs per cubic foot.

[h] Shrimp shell waste is 75–80% water; crab shell waste is about 60% water.

[i] 5–7% dry chitin in wet waste.

[j] Trucking costs will be discussed in more depth in Section 3.1.4. below. By way of illustration, a round trip of 100 miles (to and from a source of shell waste located 50 miles from a waste processor) means at least two hours travel time. Adding to this an equal amount of loading and unloading time, such a round trip will occupy the two workers in the trucking unit for half a day each. Considering only labor rates at $7.50/hour, such a round trip costs $60. At a density of 13 lbs/cubic foot a truckload of wet shrimp waste (for ordinary 18′ × 8′ × 4′ rack-body trucks) weighs only 7500 lbs, and would contain, at most, 525 lbs of dry chitin. The wet waste transport cost would therefore come to at least $60/525 lbs chitin = 11.4¢/lb chitin. This is an appreciable addition to the cost of the ultimate product. For distances longer than 50 miles, requiring more than one half-day's time for a round trip, costs would be correspondingly higher.

TABLE 3.2
STATISTICAL SURVEY PROCEDURE

Recovery of Processed Shrimp Products and Factors for Converting Them to Weight of Raw Basic Product, South Atlantic and Gulf States

	Processed Product			
Basic Product, Raw	*Headless Raw*	*Peeled Fantail Raw*	*Peeled Raw*	*Peeled Cooked*
Heads-On (Round)	62.9%	50.0%	49.0%	31.9%
Factor	1.59	2.00	2.04	3.13
Headless	100.0%	79.6%	77.9%	50.7%
Factor	1.00	1.26	1.28	1.97
Peeled	—	—	100.0%	65.1%
Factor	—	—	1.00	1.54

	Processed Product—Continued		
Basic Product, Raw	*Breaded Raw*	*Canned*	*Dried*
Heads-On (Round)	100.0%	31.2%	13.0%
Factor	1.00	3.21	7.69
Headless	159.0%	49.6%	20.7%
Factor	0.63	2.02	4.83
Peeled	204.1%	63.7%	26.5%
Factor	0.49	1.57	3.77

See note below following table.

Recovery of Processed Shrimp Products and Factors for Converting Them to Weight of Raw Product, Pacific and North Atlantic States

	Processed Product		
Basic Product, Raw	*Headless Raw*	*Peeled Raw*	*Canned*
Heads-On (Round)	57.0%	28.0%	16.0%
Factor	1.75	3.57	6.25
Headless	100.0%	49.1%	28.1%
Factor	1.00	2.04	3.56
Peeled	—	100.0%	57.1%
Factor	—	1.00	1.75

Note: The quantity of processed product multiplied by the factor listed yields the weight of basic product required to produce the processed product.

Other Conversion Factors

Item	*When Reported As*	*To Convert To:*	*Multiply By*
Oysters	Gallons of Shucked Meats	Pounds of Shucked Meats	8.75
Clams	"	"	8.75
Scallops	"	"	8.75
Oils, Fish and Whale	Gallons	Pounds	7.75
Crab Meat:			
Blue	Pounds	Live Weight	7.14
Dungeness	"	" "	4.17

From National Marine Fisheries Service. Fisheries Statistics of the U.S. 1972 Statistical Digest No. 66. Washington, D.C., 1973.

TABLE 3.2 (cont.)
STATISTICAL SURVEY PROCEDURE
Recovery of Shrimp Products and Factors for Converting Them to Heads-On Weight

Item	*South Atlantic and Gulf Catch*		*Pacific and North Atlantic Catch*	
	Percent Recovery From Heads-On Weight	*To Convert To Heads-On Weight, Multiply By:*	*Percent Recovery From Heads-On Weight*	*To Convert To Heads-On Weight, Multiply By:*
Headless:				
Brown (*Penaeus Aztecus*)	62.1	1.61	—	—
Pink (*Penaeus Duorarum*)	62.5	1.60	—	—
White (*Penaeus Setiferus*)	64.9	1.54	—	—
Royal Red (*Hymenopenaeus Robustus*)	55.6	1.80	—	—
Sea Bobs (*Xiphopenaeus Kroyeri*)	65.4	1.53	—	—
Other (Mostly *Pandalus* Species)	—	—	57.0	1.75
All Species (Weighted Average)	62.9	1.59	57.0	1.75
Peeled Fantail, Raw[1]	50.0	2.00	—	—
Peeled, Raw[1]	49.0	2.04	28.0	3.57
Peeled, Cooked[1]	31.9	3.13	—	—
Breaded, Raw (including Fantail)[1]	100.0	1.00	—	—
Dried[1]	13.0	7.69	—	—
Canned[1]	31.2	3.21	16.0	6.25

[1] Average for All Species

Note: Effective in 1962, the conversion factors listed above became the Statistics and Market News Divisions' factors for converting various shrimp products to heads-on (round) weight.

shrimp and crab and the weight of ultimate products (breaded shrimp, crab meat, etc.) for different regions of the country. The first set of columns in Table 3.3 shows the results of using these relationships to calculate the original live weight of the animals, which gives rise to the relevant[k] processed products in different states. Then, starting with these state-by-state figures, the next three sets of columns in Table 3.3 show the calculations (outlined in the previous section) of the quantities of different shellfish processed in individual 50-mile radius areas.

It is apparent from these data that the major crab processing centers are located in the middle Atlantic states, while major shrimp processing centers are on the Gulf coast, with the largest single center in the New Orleans area.

3.1.2.4 Quantities of Waste Available in Different Areas The next step is to take the live weight processing data shown in Table 3.3 and other information on the availability of shrimp heads, and to interpret these in terms of quantities of waste available in different localities. To do this, assumptions are needed about the fraction of whole live shrimp and crab weight that ends up as wet solid waste:

Assumption #3:

Waste Source	% Wet Waste/Live Weight
Crab processing	*60–75%*
Shrimp (body peeling only)	*9–22%*[l]
Shrimp (head only)	*37% (East & Gulf)* *43% (West)*

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[k] Excluded from Table 3.3 are all those processed products shown in bold face in Tables 3.1a–f — that is, those products marketed with shells on. In addition, the data for Massachusetts and Louisiana have received further adjustments. For Massachusetts, inquiries indicated that the great bulk of processed shrimp products are produced from shrimp imported from abroad already beheaded and peeled. The live weight shown in the table for this state is the live weight of local shrimp landed in 1975. For Louisiana, conversations with local individuals indicated that the last few years have seen a burgeoning of commercial crawfish processing, and we have included an estimate of the live weight of crawfish currently processed for meat.

[l] Upper value applied to that fraction of the shrimp in each area which are small enough to be landed with heads on (see discussion in text below).

For crab processing, the low value of 60% was derived by deducting maximum values of 20% of live weight for cooking loss and 20% for meat yield from the input live weight.[4] The high value of 75% solid waste/live weight follows from low assumptions of 10–15% average cooking loss and 10–15% average meat yield.[4] These percentages will undoubtedly vary for different types of equipment, processing techniques, crab species, and the season of the year. However, we believe that these limits reflect a range of reasonable expectations for the *average* waste yield for processors located within the designated areas.

For shrimp, we have chosen to separate — at least conceptually — the waste originating from body peeling and the waste originating from discarded heads. (As mentioned earlier, the availability of shrimp heads depends on local shrimping practices and must be estimated primarily from landing, rather than processing, information.) The body peeling waste, however, can be estimated from the data in Table 3.3. The low assumption of 9% waste/live weight listed above is derived from observations[4] that, for large shrimp (such as those landed most of the year in Texas), shell is about 15% of the weight of shrimp brought in without heads. Given that about 40% of the weight of a shrimp is head, the fraction of body peeling waste to total live weight is:

$$.15/(1/[1 - 4]) = .15(1 - .4) = .09$$

The higher assumption of 22% waste/live weight is based on two considerations:

- For smaller shrimp, with a larger ratio of surface/volume, the fraction of total body weight that is shell is likely to be considerably greater than for the large Texas shrimp.
- The CRESA report[3] presents data for the very small Alaskan shrimp[m], indicating that mechanical heading and peeling processes yield about 72% of the incoming live weight as solid waste (see Tables 7 and 8 of reference 3). Deducting a conventional 43% of live weight for waste originating from the head, from West Coast sources leaves about 29% of live weight as body peeling waste. We have chosen to use the somewhat more conservative value of 22% for our upper limit, however, in recognition of the fact that Alaskan shrimp are likely to be on the average smaller than shrimp taken in other small-shrimp areas of the U.S. (Maine, Massachusetts, and the West coast).

Finally, we come to the problem of shrimp *heads*. Practices of heading shrimp at sea vary with geographic area, shrimp species and size, length of time for shipboard storage, abundance of the catch, and acceptability of head-on shrimp at dockside. Shrimp with heads on are highly perishable and must be landed quickly, before enzymes in the head ruin the catch. Head-on shrimp also bring a lower price when landed. Very small (especially Arctic) shrimp are landed with heads on and processed by machines because of the impracticability of manual heading at sea. Small shrimp caught near shore on short excursions from port, as in the waters off Louisiana, are also often landed with heads on. By contrast, larger shrimp that are taken on longer cruises must be headed at sea, where the heads are discarded. In certain areas, such as Key West, some packers have the facilities and manual labor available for heading shrimp at dockside and will accept this responsibility at a discounted price. Others in the same area cannot or will not. At the same time, shrimpers in the area may choose to fish only for larger shrimp and do the heading before landing, while others will take their chances with larger catches of smaller shrimp. At times, the catch volume of large shrimp is too great to process on board, and the trip is shortened by a hasty return to port with a heads-on catch.

Such variability, and the omission of detailed data on heads from state and Federal statistics, imposes a handicap that was partly relieved by a company-by-company survey of the South Florida area and a port-by-port survey of northern Florida, Georgia, Mississippi, Louisiana, and

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[m] In general, colder waters are associated with smaller shrimp. Those in Alaska are reported to be between "350 to 450 per lb on a peeled weight basis," which may correspond to about 70 to 90 per pound on the more standard live-weight basis.

TABLE 3.3
Live Weight of Processed Shellfish Which May be

	Millions of Lbs. Processed					
Region (State)	*A* *Shrimp*	*B* *B. Crab*	*C* *D. Crab*	*D* *N. Lobster*	*E* *Rock Crab*	*F* *Crawfish*
New England						
Maine	19.28			(.20)[a]	(.06)[a]	
Mass	4.59[c]			(.38)[a]		
Total	63.51			(.58)[a]	(.06)[a]	
Middle Atlantic & Chesapeake						
Maryland & Del.		23.21				
Virginia	.18	26.21				
Total	.18	49.42				
South Atlantic						
N. Carolina		21.99				
S. Carolina	.19	3.50				
Georgia	16.02	13.71				
Florida (E)	13.18	5.57				
1.						
2.						
Total	29.49	44.77				
Gulf						
Florida (W)	56.88	10.71				
1.						
2.						
3.						
Alabama/Miss.	11.61	6.07				
Louisiana	51.84	10.07				
1.						
2.						≈4[d]
Texas	55.90	7.85				
1.						
2.						
3.						
Total	176.23	34.70				4
Pacific Coast						
Washington	8.26		6.27			
(Oregon/Washington)	(18.36)		(10.23)			
California	16.65		4.04			
1.						
2.						
3.						
Total	35.08		14.35			
Alaska[b]	26.39		23.6		.32	
				King Crab	~74.0	
				Tanner Crab	~26.3	

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*This table summarizes the live weight of different shellfish processed in such a way as to yield chitin-bearing wastes in different geographic locations. For assumptions and data sources, see the accompanying explanations in the text. For definition of the geographic areas considered within each state, see the maps in Appendix A.

[a] Processed meat weight.

Chitin Sources in Different Areas—1972*

Total # Processing Plants						*Plants Within 50-Mile Radius Areas*						*Millions of Lbs. Processed Within 50-Mile Radius Areas*					
A	*B*	*C*	*D*	*E*	*F*	*A*	*B*	*C*	*D*	*E*	*F*	*A*	*B*	*C*	*D*	*F*	*F*
27			24	5		22			16	3		15.71			(.13)	(.04)	
11			31			11			30			4.59			(.37)		
												59.14			(.50)[b]	(.04)[b]	
	44						41						21.63				
3	37					3	36					.18	25.50				
												.18	47.13				
	28						23						18.06				
4	4					3	4					.14	3.50				
5	8					5	8					16.02	13.71				
10	15																
						1	9					1.32	3.34				
						6	3					7.91	1.11				
												25.39	39.72				
31	21																
						11	5					20.18	2.55				
						14	10					25.69	5.10				
						5						20.08	6.07				
23	24					23	24										
64	28				22												
						51	20				6	41.31	7.19				
						7	8				13	5.67	2.88				≈4[d]
36	11																
						10	7					15.52	5.00				
						12	3					18.63	2.14				
						13	0					20.19	0.00				
												167.99	30.93				4
5		10				4		7				6.61		4.39			
19		31				7		10				6.76		3.30			
15		7															
						9		0				9.99		0.00			
						3		4				3.33		2.31			
						1		2				1.11		1.15			
												27.80		11.15			
											Grand Totals:	281.30	117.78	11.15	(.50)	(.04)	4

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[b] 1970 data from Reference 3.

[c] 1975 landings of local shrimp (see text for explanation).

[d] Our estimate for recent years (see text).

TABLE 3.4
Estimation of Quantities of Shrimp Head Waste Available in Different Areas

Area	*Annual Shrimp Landings (Millions of Lbs)*	*Estimated % Of Landings With Heads On*	*Average % Of Live Weight Which is Head*	*Head Waste Per Year (Millions of Lbs)*	*Remarks*
Maine	16.57	100	43	7.12	
Massachusetts	4.59	100	43	1.97	1974 landing data—Essentially all landings of native shrimp are in Gloucester. Much more shrimp is imported from abroad (e.g., India) already beheaded and peeled.
North Carolina	5.56	60–70	37	1.23–1.44	Estimated percent of heads on is made by analogy with Georgia/South Carolina.
South Carolina	8.09	60–70	37	1.80–2.10	Percent of heads on inferred from conversation with NMFS Office in Savannah. South Carolina shrimp shipped to Georgia for processing.
Georgia	7.26	60–70	37	1.63–1.91	"
Florida E#1	1.24	10–15	37	0.05–0.07	1974 landing data—Represents the sum of approximately 844,000 lbs landed at Cape Canaveral and 393,000 lbs landed at New Smyrna Beach. Other landings at St. Augustine and elsewhere are too far to the north to be included as a source of heads.
Florida E#2	1.55	10–15	37	0.06–0.09	1974 landings assumed to be in Miami area.
Florida-Key West	11.23	70	37	2.91	1974 landing data—Shrimp landed in Key West are beheaded and then trucked to Tampa (Fla. W#1) for further processing.
Florida W#1	3.36	10	37	0.12	1974 landing data for Tampa/Tarpon Springs/St. Petersburg area.
Florida W#2	3.96	50	37	0.73	1974 landing data for Apalachicola area. Mainly in-shore fishery harvesting relatively small shrimp.
Ala./Miss./Fla.	25.50	30–45	37	2.83–4.25	Total 1972 landings for Alabama and Mississippi. In contrast with Louisiana, Alabama and Mississippi have year-round rules restricting the harvest of very small shrimp.
Louisiana #1	66.17	40–65	37	9.79–15.91	Small shrimp with about 80% heads on make up the Spring catch—which is approximately one-half the annual total catch. Heads apportioned between Louisiana areas in proportion to the numbers of processing plants.
Louisiana #2	9.08	40–65	37	1.34–2.18	
Texas #1				~1.20	
Texas #2	97.58	10	37	~1.20	Landings in Texas are very large, but almost all without heads.
Texas #3				~1.20	
West Coast Areas:					All small shrimp landed with heads on for mechanical beheading and peeling. Calculations based on the live weight necessary for the production of the processed products made in different areas (See Table 3.3).
California #1	—	100	43	4.30	
California #2	—	100	43	1.43	
California #3	—	100	43	0.48	
Oregon/Wash.	—	100	43	2.91	
Washington	—	100	43	2.84	
Alaska (whole State)	—	100	43	11.35	

TABLE 3.5
Potential Waste and Potential Products in Different Areas*

	Millions of Lbs of Wet Waste of Different Types*				Millions of Lbs of Potential Products of Different Types		
Area	*Shrimp Body Peelings***	*Shrimp Head Waste*	*Crab Waste*	*Total Waste*	*Adventitious Protein*	*Total Protein*	*Total Chitin*
Maine	1.41–3.46	7.12	.10– .13	8.63– 10.71	.371– .720	.538– 1.03	.274– .553
Massachusetts	.41–1.01	1.97	.22– .28	2.6 – 3.26	.118– .230	.173– .325	0.87– .171
Md./Del.	0	0	12.98–16.22	12.98– 16.22	.935– 1.82	1.56 – 2.27	.675– .973
Virginia	.02– .04	0	15.3 –19.13	15.32– 19.17	1.10 – 2.15	1.84 – 2.68	.797–1.15
N. Carolina	0	1.23– 1.44	10.8 –13.55	12.03– 14.99	.837– 1.61	1.37 – 2.03	.595– .876
S. Carolina	.01– .03	1.80– 2.10	2.10– 2.63	3.91– 4.76	.224– .433	.357– .568	.158– .252
Georgia	1.44	1.63– 1.91	8.23–10.28	11.3 – 13.63	.738– 1.38	1.20 – 1.76	.550– .798
Florida E#1	.12	.05– .07	2.00– 2.51	2.17– 2.70	.153– .294	.253– .370	.112– .162
Florida E#2	.71	.06– .09	.67– .83	1.44– 1.63	.090– .149	.141– .196	.075– .102
Florida-Keys	0	2.91	0	2.91	.116– .189	.169– .273	.079– .127
Florida W#1	1.82	.12	1.53– 1.91	3.47– 3.85	.217– .349	.336– .461	.181– .243
Florida W#2	2.31–3.98	.73	3.06– 3.83	6.10– 8.54	.379– .755	.594– 1.00	.304– .530
Ala./Miss./Fla.	1.87–3.93	2.83– 4.25	3.64– 4.55	8.34– 12.73	.480– 1.06	.757– 1.43	.367– .724
Louisiana #1	3.72–7.21	9.79–15.91	4.31– 5.39	17.82– 28.51	.910– 2.14	1.38 – 2.97	.689–1.51
Louisiana #2	.51– .99	1.34– 2.18	4.13– 5.16	5.98– 8.33	.380– .789	.614– 1.03	.278– .472
Texas #1	1.40	~1.20	3.00– 3.75	5.60– 6.35	.342– .596	.542– .778	.264– .372
Texas #2	1.68	~1.20	1.28– 1.61	4.16– 4.49	.234– .376	.358– .506	.190– .263
Texas #3	1.82	~1.20	0	3.02	.150– .205	.215– .295	.131– .175
California #1	.90–2.20	4.30	0	5.2 – 6.5	.222– .434	.321– .623	.165– .337
California #2	.30– .73	1.43	1.39– 1.73	3.12– 3.89	.174– .338	.274– .449	.127– .216
California #3	.10– .24	.48	.69– .86	1.27– 1.58	.074– .144	.119– .189	.054– .089
Oreg./Wash.	.61–1.49	2.91	1.98– 2.48	5.5 – 6.88	.293– .571	.455– .769	.214– .377
Washington	.59–1.45	2.84	2.63– 3.29	6.06– 7.58	.336– .655	.528– .872	.245– .420
Alaska (whole state)	2.38–5.81	11.35	74.34–92.93	88.07–110.1	5.94 –11.55	9.77 –14.66	4.30 –6.46
Total (excluding Alaska)					8.9 –17.4	14.1 –22.9	6.6 –10.9

*See text, Assumption #3 and Tables 3.3 and 3.4 for data base and calculation methods.

**Upper limits assume that small shrimp landed with heads on yield 22% peeling waste/live weight. Lower limits are 9% of live weight of shrimp processed in different areas.

Texas. Table 3.4 contains estimates, inferences, and conclusions drawn from conversations with local National Marine Fisheries Service personnel, shrimp packers, processors, and other knowledgeable individuals on the quantities of shrimp landed in different areas with and without heads on.

Bringing all of these computations together, the first set of columns in Table 3.5 summarizes the quantities of wet waste likely to be available in different geographic areas. The second set of columns is constructed with composition data discussed in the following section.

3.1.3 Composition of Wastes and Potential Quantities of Different Products from Individual Areas

This section considers selected information and assumptions on the detailed composition of shell waste originating from various sources, and shows how these (and data on waste availability) translate into estimated quantities of chitin and protein potentially producible in different localities.

The major components of shell waste are water, chitin, protein, and calcium carbonate. The protein is present in two forms:

- In remnants of flesh and connecting tissue attached to the shell
- protein firmly complexed with chitin and calcium carbonate as an integral part of the shell

The first type of protein[n] is called *adventitious protein* and may be separated from the remainder of the shell waste by available meat-bone separators (such as Baader, Yanagiya, Bibun). The second type of protein can only be separated from the chitin by chemical means -- most frequently by treatment with dilute base solution.

As with other types of data important to the analysis of the economics of chitin supply and demand, there has been no systematic survey to ascertain the chemical composition of shell wastes from different areas. Rather widely discrepant data are available from a number of sources[3-7] on chitin and occasionally on protein contents of shell and/or shellfish wastes of various kinds, but comprehensive and reliable comparative analyses are not available. Such a survey might be a valuable step toward further exploration of the potential chitin supply — if further exploration is deemed to be warranted.

We have used the primary data we consider most reliable, (mainly, the operating experience of chitin production from shrimp shell waste in Texas, some preliminary commercial data on blue crab waste from the Atlantic seaboard, and the protein analyses of shrimp heads and hulls by the Bough group[5]) to construct reasonable ranges of expectation for the shellfish wastes available nationally. In the tables constituting Assumption #4 on the following page, the numbers listed on the left hand side of the ranges represent reasonable but pessimistic assessments of probable composition (i.e., lesser amounts of the valuable components, chitin and adventitious protein), and the numbers listed on the right hand side of the ranges represent reasonable but optimistic assessments of composition:

Assumption #4: Materials recoverable[o] from wet waste:

A. Dry Weight Basis[p]

	Shrimp Body Peeling Waste	Shrimp Head Waste[o]	Crab Waste
Chitin	*27%*	*13.5–17.5%*	*13–15%*
Protein — Total	*40%*	*29–37.5%*	*30–35%*
Adventitious[q] protein	*(28%)*	*(20–26%)*	*(18–28%)*
Firmly bound protein	*(12%)*	*(9–10%)*	*(12–7%)*
Ash (Calcium carbonate)	*33%*	*25–27%*	*50%*
Soluble material and other (e.g. fat, digested protein)	*0*	*32.5–20%*	*7–0%*
Dry Total	*100%*	*100%*	*100%*

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[n] Strictly speaking, this is a misnomer. A better term, recognizing that meat is not wholly protein, would be *proteinaceous tissue*. The misnomer, preserved by convention, alludes to the protein content, the basis on which the product ultimately is priced and sold.

[o] Chitin and protein percentages have been adjusted in the case of shrimp head waste to reflect our guess that, due to digestive enzymes in shrimp heads, only about half to three quarters of the protein and chitin may be recoverable. This expectation was formed partly from qualitative reports of experimentation with chitin extraction in Texas[4], and partly from the observations of shrimp head protein autolysis reported by Bough[5]. Before the recoverability adjustment, our expectation for the composition of shrimp head waste is: Chitin — 20%; Total Protein — 43%, Adventitious protein — 30%; Firmly bound protein — 13%; Calcium carbonate — 25%; Other — 12% (all on a dry weight basis).

[p] In this section of the table, percentages refer to the fraction of the total dry weight of the waste made up by individual dry components.

B. Wet Weight Basis[r]

	Shrimp Body Peeling Waste	Shrimp Head Waste	Crab Waste
Water	*80–75%*	*80–75%*	*60%*
Chitin	*5.4–6.75%*	*2.7–4.38%*	*5.2–6%*
Protein — Total	*8–10%*	*5.8–9.38%*	*12–14%*
Adventitious[q] *protein*	*(5.6–7%)*	*(4–6.5%)*	*(7.2–11.2%)*
Firmly bound protein	*(2.4–3%)*	*(1.8–2.5%)*	*(4.8–2.8%)*
Ash (Calcium carbonate)	*6.6–8.2%*	*5–6.75%*	*20%*
Soluble material and other (e.g. fat, digested protein)	*0*	*6.5–4.5%*	*2.8–0%*
Wet Total	*100%*	*100%*	*100%*

Utilizing these assumptions about the quantities of chitin and protein potentially producible from different kinds of wastes, Table 3.5 (p. 29) shows the amounts of each product that might be derived from the wastes collectible in different areas of the country. *For this, and subsequent tables, lower values of the ranges were derived by multiplying the more pessimistic assumptions about percentage composition with the lower set of assumptions about the quantities of wastes available. Conversely, the higher values of the ranges were derived by multiplying the more optimistic assumptions about percentage composition with the more optimistic assumptions on the quantities of different wastes available.*

3.1.4 Costs of Producing Dried Protein and Shell Waste Residual in Different Areas

This section analyzes the economic costs and benefits of shell waste residual/protein production from the standpoint of a large, centrally located shellfish processor in each of the areas of the country designated in Section 3.1.2. The question addressed is, "What long-term price of shell waste residual would be necessary in order to make the start of production a *good investment*."[s]

The estimates we have made of different cost and benefit[t] components can be divided into two broad groupings:

- *Process-based cost estimates* have been made for those operating expenses whose size is related in some simple way to the quantity of material that passes through a particular process: i.e., purchase of wet waste; trucking costs; labor, fuel, and acid for the protein separation and drying steps; credits for protein sale and waste disposal costs saved.
- *System-based cost estimates* have been made for all costs that are fixed in the short run and/or are not simply relatable to the quantity of material that passes through a particular process: i.e., amortization of capital equipment and minimum required return on investment. (For this section, these are simply the allocatable capital costs.)

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[q] *Adventitious protein* is the protein that is removable from the shell waste by purely mechanical means (Baader or Yanagiya meat-bone separators for wet waste, or possibly a screening process for crab waste after drying).

[r] In this section of the table, percentages refer to the fraction of the total wet weight of the waste made up by individual dry components.

[s] We define a *good investment* as one which provides, at minimum, an expected return on capital equal to the return on other potential investments for the firms concerned (after adjustment for differential risk). For purposes of analysis, we shall tentatively assume that the minimum required annual return is between 20–40% of total capital invested (before tax).

[t] The *benefits* referred to are (1) revenue realized from the sale of protein, and (2) solid waste disposal costs saved by the use of the wet waste.

In all cases, the costs and benefits are expressed in terms of their contribution to the minimum required net cost of shell waste residual (cents per pound) for each individual area of potential production.

Many of the types of costs are greatly dependent on the scale of production in an individual area; other things being equal, larger operations can often be expected to produce with lower unit costs.[u] On the other hand, for each individual area there will be some trade off between potential cost reductions from larger-scale operation and the increased costs involved in purchasing and trucking larger quantities of waste to a single location for processing. As a first effort toward understanding how this trade off may be made, for each of the selected areas of production we analyze costs based on two levels of production (at one-third of an area's potential yield, and at full production) under the following assumption:[v]

> *Assumption #5: In each area, there is one large shellfish processor (or a group of shellfish processors in very close proximity) that would have one third of the area's waste available for its own use with no cost for transportation and with a savings of about \$5/ton in alternative disposal costs. The remaining waste in each area would be available from other shellfish processors with transportation cost plus \$0–20/ton purchase cost.*

In other words, we first estimate the costs of production of shell waste residual from the standpoint of a single large shellfish processor in each area processing only its own waste — assumed to be equal to one third of the total waste potentially available in that area. Second, we estimate the incremental costs of producing shell waste residual from the rest of the waste theoretically available in each area, balancing off the benefits of increased scale with the costs of wet waste transport and \$0–20/ton purchase cost.

Table 3.6 shows the overall quantities and composition of the shell waste residual producible in each area.[w] (The quantities of the coproduct adventitious protein for each area were given in Table 3.5). It should be noted that the shell waste residual that can be made in areas with predominantly crab waste available (e.g. Virginia, Maryland) is substantially lower in chitin and higher in calcium carbonate than the shell waste residual available in areas with predominantly shrimp waste available (e.g. Maine, Texas #3). Later, it will be seen that this difference leads to differential production costs in the ultimate manufacturing of chitosan (Section 3.1.5).

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[u] For example, the capital cost of dryers is not directly proportional to dryer capacity, but rather rises approximately with the two-thirds power of dryer capacity. Additionally, a worker can tend a larger dryer with about the same expenditure of effort as would be required for a smaller dryer, leading to lower unit labor costs for the larger dryer.

[v] This particular assumption is one that will particularly require reassessment on the basis of each area's individual situation prior to investment decisions.

[w] The amount of shell waste residual (SWR) for each area was computed simply as the total dry weight of the available waste minus the dry weight of the recoverable adventitious protein. For the three sources of wet waste, the quantities of dry shell waste residual available are:

Shrimp body peeling waste: $Q_{SWR} = (.144-.18)(Q_{wet\ waste})$
Shrimp head waste: $Q_{SWR} = (.095-.135)(Q_{wet\ waste})$
Crab waste $Q_{SWR} = (.288-.3)(Q_{wet\ waste})$

The composition of the shell waste residual produced from the three sources would be expected to be (100% dry weight basis):

	% chitin	% $CaCO_3$
$SWR_{shrimp\ body\ peelings}$	37.5	45.8
$SWR_{shrimp\ head}$	28.4–32.1	52.6–49.5
SWR_{crab}	17.3–20.8	66.7–69.4

In actual operations, the quantity of shell waste residual might be expected to be somewhat less than that shown above, because some chitin-bearing material would wind up mixed with the adventitious protein fraction due to imperfect separation. However, this would be a relatively modest subtraction if, as anticipated, 70% or more of the dry weight of the protein fraction is in fact protein.

TABLE 3.6

	*Shell Waste Residual Potentially Available in Different Areas (Millions of Lbs.)***				*Composition of Shell Waste Residual**	
Area	*From Shrimp Body Peelings*	*From Shrimp Heads*	*From Crab Wastes*	*Total Shell Waste Residual*	*% Chitin*	*% $CaCO_3$*
Maine	.203– .623	.676– .961	.029– .039	.908– 1.623	30.0–34.0	48.5–51.8
Massachusetts	.059– .182	.187– .266	.063– .084	.310– .532	27.2–32.6	50.7–55.7
Md./Del.	0	0	3.738– 4.866	3.738– 4.866	17.3–20.8	69.4
Virginia	.003– .007	0	4.406– 5.739	4.409– 5.746	17.3–20.9	69.4
N. Carolina	0	.117– .194	3.110– 4.065	3.227– 4.259	17.6–21.5	68.3–69.0
S. Carolina	.001– .005	.171– .284	.605– .789	.777– 1.087	19.3–24.5	63.0–66.4
Georgia	.207– .259	.155– .258	2.37 – 3.08	2.732– 3.601	19.0–23.3	65.5–67.3
Florida E#1	.017– .022	.005– .009	.347– .753	.369– .784	17.8–22.1	67.6–68.8
Florida E#2	.102– .128	.006– .012	.193– .249	.301– .389	23.3–27.6	59.6–62.4
Florida-Keys	0	.276– .393	0	.276– .393	28.4–32.1	49.5–52.6
Florida W#1	.262– .328	.011– .016	.441– .573	.714– .917	23.7–28.0	59.2–61.9
Florida W#2	.333– .716	.069– .099	.881– 1.149	1.283– 1.964	22.2–28.5	58.3–63.6
Ala./Miss./Fla.	.269– .707	.269– .574	1.048– 1.365	1.586– 2.646	21.8–28.7	57.4–63.7
Louisiana #1	.536–1.298	.930–2.148	1.24 – 1.62	2.707– 5.063	24.2–30.6	53.8–60.3
Louisiana #2	.073– .178	.127– .294	1.189– 1.548	1.390– 2.021	19.0–24.6	63.4–67.2
Texas #1	.202– .252	.114– .162	.864– 1.125	1.180– 1.539	21.0–25.5	62.3–64.8
Texas #2	.242– .302	.114– .162	.387– .483	.725– .947	24.7–28.9	57.3–60.3
Texas #3	.262– .328	.114– .162	0	.376– .490	34.7–35.7	47.1–47.9
California #1	.130– .396	.409– .581	0	.538– .977	30.6–34.3	48.0–51.0
California #2	.043– .131	.136– .193	.400– .519	.579– .843	20.7–26.9	59.9–64.7
California #3	.014– .043	.046– .065	.199– .258	.259– .366	19.8–25.6	61.9–66.0
Oreg./Wash.	.088– .268	.276– .393	.343– .744	.707– 1.405	21.7–29.7	55.3–63.4
Washington	.085– .261	.270– .383	.757– .987	1.112– 1.631	20.8–27.0	59.6–64.6
Alaska (whole state)	.343–1.046	1.078–1.532	12.88 –27.88	14.30 –30.46	18.0–23.1	65.8–68.5
TOTALS (excluding Alaska)	3.13 –6.43	4.48 –7.61	22.6 –30.0	30.2 –44.1		

*The fraction of the shell waste residual which is neither chitin nor calcium carbonate is strongly-bound protein.

**100% dry weight basis

3.1.4.1 Costs of One-Third Potential Production From Wastes At a Single Site in Each Area

The results of these computations are presented in Table 3.7. Below we discuss the assumptions and calculation procedures leading to the cost estimates in each column of this table.

Process-based cost estimates

- Credit for alternative disposal
- Labor cost for separation of wet waste into protein and residual fractions

These two elements of cost are treated together, since they both vary directly with the quantity of wet waste that is processed for each pound of shell waste residual. By assumption #5 above (p.32) the alternative disposal credit was postulated to be $5/ton (.25¢/lb) of wet waste. The resulting credit toward the ultimate cost of each pound of shell waste residual in each area is therefore

$$(.25¢/\text{lb wet waste})\left(\frac{\text{\# lbs wet waste processed}}{\text{\# lbs shell waste residual produced}}\right)$$

On the other hand, the labor input required for separating the wet waste into its components (wet protein and residual) appears to be quite considerable. An informant familiar with the process[4] considers it advisable to assign three people to the operation.[x] To calculate costs, we make the following assumptions about throughput and labor cost:[y]

> *Assumption #6: With a larger model of meat-bone separator (either Baader or Bibun), a three-man crew can process 5000 lbs of wet waste per hour.*
>
> *Assumption #7: Labor costs (including all benefits and administrative overhead expenses) may be between $13,000–18,000/year-equivalent, or $6.50–9.00/hour of operation of the separator.*[z]

Given this, the cost of processing each pound of wet waste is

$$\frac{(\text{3 people})(\$6.50\text{–}9.00/\text{person-hour})}{\text{5000 lbs wet waste/hr}} = .39\text{–}54¢/\text{lb wet waste}$$

Subtracting the .25¢/lb wet waste disposal credit from above, the net cost is .14–.29¢/lb wet waste, or, in terms of the ultimate cost of producing each pound of shell waste residual:

$$(.14\text{–}.29¢/\text{lb wet waste})\left(\frac{\text{\# lbs wet waste processed}}{\text{\# lbs shell waste residual produced}}\right)$$

The variations that can be seen between areas in the results of this calculation shown in Table 3.7 arise from the fact that the number of pounds of wet waste that must be processed to produce each pound of dry shell waste residual is larger for shrimp wastes than for crab wastes (shrimp wastes have a larger moisture content).

- Wet waste transport

By assumption #5 (p. 32) the third of the waste in each area that we are now considering is available on site without need for appreciable transportation.

- Credit from the sale of mechanically-separated protein
- Cost of labor, acid, and fuel for precipitating and drying the mechanically-separated protein

One the the most prominent uncertainties in our entire analysis of the economics of shellfish waste utilization is the price at which the dried protein product can be sold. It seems reasonable to assume that the protein price will be closely dependent on the price of protein from traditional fish meal[aa] but fish meal prices are highly volatile. Figure 3.2 shows the history of the

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[x] One worker each is thought to be needed to operate the systems conveying wet waste to the grinder and conveying the protein to a slurry tank for acid precipitation. The third worker would be primarily in a supervisory role, but would be available to help the others with control of the process as needed.

[y] The labor cost assumption is another assumption which should be reassessed in the light of prevailing wage rates, benefit costs, and overhead charges for firms contemplating investment.

[z] By reducing the cost to an hourly rate, we assume that during any time in which the three-person crew is not needed in the separation operation, they can be productively employed in other aspects of the shell waste processor's business (this flexibility is one advantage of carrying out the waste utilization operations in the context of an existing business.)

[aa] Some experiments are reported to suggest that the protein from crab waste may contain an as yet unidentified growth factor that may cause it to be more valuable in animal feeds than traditional fish meal,[4] but this will require further investigation. Another possibility is that the protein may be able to sell at some premium over the price of fish meal protein because the shrimp and, to a lesser extent, crab protein also contain astaxanthin, a red pigment that produces the desirable color of salmon. Salmon grown by aquaculture techniques must be provided a source of astaxanthin or their meat will sell at a discount. Some quantities of shellfish waste are reportedly purchased by some aquaculture firms for this purpose at present. Other specialty animal feed applications also may provide lucrative markets.

TABLE 3.7

Costs of Shell Waste Residual (¢/lb) Assuming:

1) 1/3 of the total waste in each area is available to an existing shellfish processor
2) Mechanically separated and dried protein will sell for 23.3–30¢/lb. 100% protein equivalent (equal to a price of 14–18¢/lb. of fishmeal with 60% protein)

		Costs: ¢/lb Shell Waste Residual						
Area	*Quantity of Shell Waste Residual lbs × 10⁶*	*Cost of Labor for Protein Separation Less Disposal Credit*** Hi Q* Lo Q**	*Transport of wet waste*	*Credit for Protein Sale Less Labor and Fuel Cost for Protein Drying***	*Shell Waste Residual Drying: Labor and Fuel**	*10–20% Depreciation + 20–40% Return on Capital Investment**	*Total Cost ¢/lb SWR**	*Total Cost ¢/lb. of Chitin in Shell Waste Residual**
Maine	.303– .541	0.9–2.8	0	(10.1–5.9)‡	.8–2.3	5.1–22.2	(3.3)–21.4	(9.7)– 66
Massachusetts	.103– .177	0.8–2.4	"	(10.0–5.5)	.8–2.3	15.6–65.2	7.2 –64.4	22 –237
Md./Del.	1.246– 1.622	0.4–1.0	"	(10.0–4.1)	.3–1.2	3.1– 8.2	(6.2)– 6.3	(30) – 36
Virginia	1.470– 1.915	0.4–1.0	"	(10.1–4.2)	.3–1.0	2.9– 7.8	(6.4)– 5.6	(31) – 32
N. Carolina	1.076– 1.420	0.5–1.0	"	(10.0–4.2)	.4–1.4	3.3– 8.8	(5.8)– 7.0	(27) – 46
S. Carolina	.259– .359	0.6–1.5	"	(9.7–4.1)	.8–2.3	7.7–25.9	(0.6)–26	(2.5)–134
Georgia	.911– 1.20	0.5–1.2	"	(9.2–3.9)	.4–1.6	3.5– 9.3	(4.8)– 8.2	(21) – 43
Florida E#1	.123– .261	0.5–1.7	"	(9.1–3.9)	.8–2.3	10.6–54.6	2.8 –55	12.7 –305
Florida E#2	.100– .129	0.6–1.4	"	(9.2–4.3)	.8–2.3	21.4–67.2	13.6 –67	50 –284
Florida Keys	.092– .131	1.1–3.0	"	(11.1–6.2)	.8–2.3	21.7–73.0	12.5 –72	39 –252
Florida W#1	.238– .306	0.6–1.4	"	(9.1–4.5)	.8–2.3	9.0–28.2	1.3 –27	4.6 –115
Florida W#2	.458– .655	0.6–1.4	"	(9.2–4.3)	.8–2.3	4.2–14.7	(3.6)–14.1	(12.6)– 63
Ala/Miss/Fla.	.529– .882	0.7–1.5	"	(10.0–4.5)	.6–2.3	3.9–12.7	(4.8)–12	(16.7)– 55
Louisiana #1	.902– 1.688	2.0–3.7	"	(11.0–5.7)	.3–1.2	3.2–11.5	(5.5)–10.7	(17.9)– 45
Louisiana #2	.463– .674	0.6–1.3	"	(9.5–3.9)	.8–2.3	4.2–14.5	(3.9)–14.2	(15.9)– 75
Texas #1	.393– .513	0.6–1.4	"	(9.3–4.1)	.8–2.3	5.4–17.1	(2.5)–16.7	(9.8)– 79
Texas #2	.242– .316	0.7–1.6	"	(9.4–4.5)	.8–2.3	8.7–27.8	0.8 –27.2	2.8 –110
Texas #3	.125– .163	0.8–2.3	"	(9.7–5.8)	.8–2.3	16.9–53.8	8.8 –53	25 –152
California #1	.179– .326	1.0–2.8	"	(9.9–5.8)	.8–2.3	8.5–37.5	0.4 –37	1.2 –119
California #2	.193– .281	0.7–1.5	"	(9.2–4.0)	.8–2.3	9.8–34.8	2.1 –35	7.8 –167
California #3	.086– .122	0.6–1.4	"	(9.2–3.8)	.8–2.3	22.6–78.1	14.8 –78	58 –392
Oregon/Wash.	.236– .468	0.7–2.2	"	(9.5–4.2)	.8–2.3	5.9–28.5	(2.1)–29	(7.1)–132
Washington	.371– .544	0.7–1.6	"	(9.2–4.0)	.8–2.3	5.1–18.1	(2.6)–18	(9.6)– 87
Alaska (whole state	4.767–10.15	0.5–1.7	"					

*For each column, the number on the left represents the cost resulting from the most optimistic highest quantity and lowest cost assumptions, and the number on the right represents the cost resulting from the most pessimistic assumptions.

‡Numbers in parentheses are negative costs (credits).

**Revenue from protein sales minus labor, acid, and fuel to run the equipment. The left number in each entry results from assuming a protein price of 30¢/lb. of 100% protein and optimistically low operating production costs (see text). The right number in each entry results from assuming a protein price of 23.3¢/lb. of 100% protein and pessimistically high operating production costs. (See text).

***Assuming three person hours per hour of operation ($6.50–9.00 cost per person-hour) processing 5,000 lbs of wet waste per hour = .39–54¢/lb. of wet waste processed. Deducting $5/ton (.25¢/lb) disposal credit, net cost through the separation step is .14–.29¢/lb of wet waste.

selling price (in constant dollars)[bb] of 60% protein fish meal from mid-1968 to the present. The very high prices that prevailed from early 1973 throughout the middle of 1975 were due to a failure of the Peruvian anchovy harvest. Unfortunately, we do not have any special insight into the future behavior of the Peruvian anchovy fishery or the likely utilization of its product. It has been suggested[cc] that protein from Peruvian anchovies could be better utilized in reducing the deficit in protein available for direct human consumption in the third world rather than for feeding animals in the U.S. However, it is unlikely that there will be such a reallocation of world protein resources in the near future.

For purposes of analysis, we have calculated two different average protein prices from the data shown in Figure 3.2. The lower average price ($280 per ton, or 14¢/lb of 60% protein fish meal = 23.3¢/lb on a 100% protein equivalent basis) was computed after excluding the unusual period of anchovy shortage and high prices. The higher average price ($360 per ton, or 18¢/lb of 60% protein fish meal = 30¢/lb on a 100% protein equivalent basis) was computed utilizing the prices of the entire period. The 23.3–30¢/lb range is our low-high expectation for future 100% protein-basis prices.

From this operating revenue realized by the sale of protein, one must deduct the operating costs for acid, labor, and fuel used in protein precipitation and drying. The first component, acid, helps to precipitate any protein that might tend to stay in solution and, ideally, promotes the maximum degree of dewatering prior to entry of the protein into the dryer.[dd] Current experience with wet separation of crab protein[4] suggests that about one-sixth of a liter (.43 lbs) of concentrated hydrochloric acid is required per pound of 70% protein product ultimately produced. The cost of this quantity of acid is not large, but the relatively higher costs of acid in the West (and to a lesser extent in the Northeast)[ee] introduces a slight regional differential into this process cost:

		Region		
		South	*Northeast*[ff]	West Coast
acid cost	$/ton HCl	40	50	65
	¢/lb HCl	2	2.5	3.25
¢/lb 66% protein cost for acid (.43 lbs HCl/lb 70% protein)		.9	1.1	1.4
¢/lb protein cost for acid (100% protein basis)		1.3	1.6	2.1

[bb] Data were collected from various issues of *Chemical Marketing Reporter* over the years. The quoted prices were converted to April 1976 dollars with the wholesale price index for all commodities.

[cc] See for example the writings of Paul Ehrlich such as *The Population Bomb.*

[dd] Dewatering may be carried out with a combination of a rotary vacuum filter and a screw press which feeds the material directly into the dryer at what is expected to be a moisture content of no more than 80%. As will be seen below, the economics of the drying operation are highly dependent on the moisture content of the feed.

[ee] Acid costs for various locations were obtained from a number of suppliers for Los Angeles, Tacoma, Washington, Boston, West Virginia, and Delaware. As of this writing, acid supplies are reportedly tight and prices may be volatile. (In Section 3.1.5 below, the regional differential will figure importantly in site selection for the process of converting shell waste residual into chitosan because the demineralization step requires considerable quantities of acid.) The reader may wish to check with suppliers of HCl for information on current conditions of acid availability and cost.

[ff] Massachusetts and Maine only.

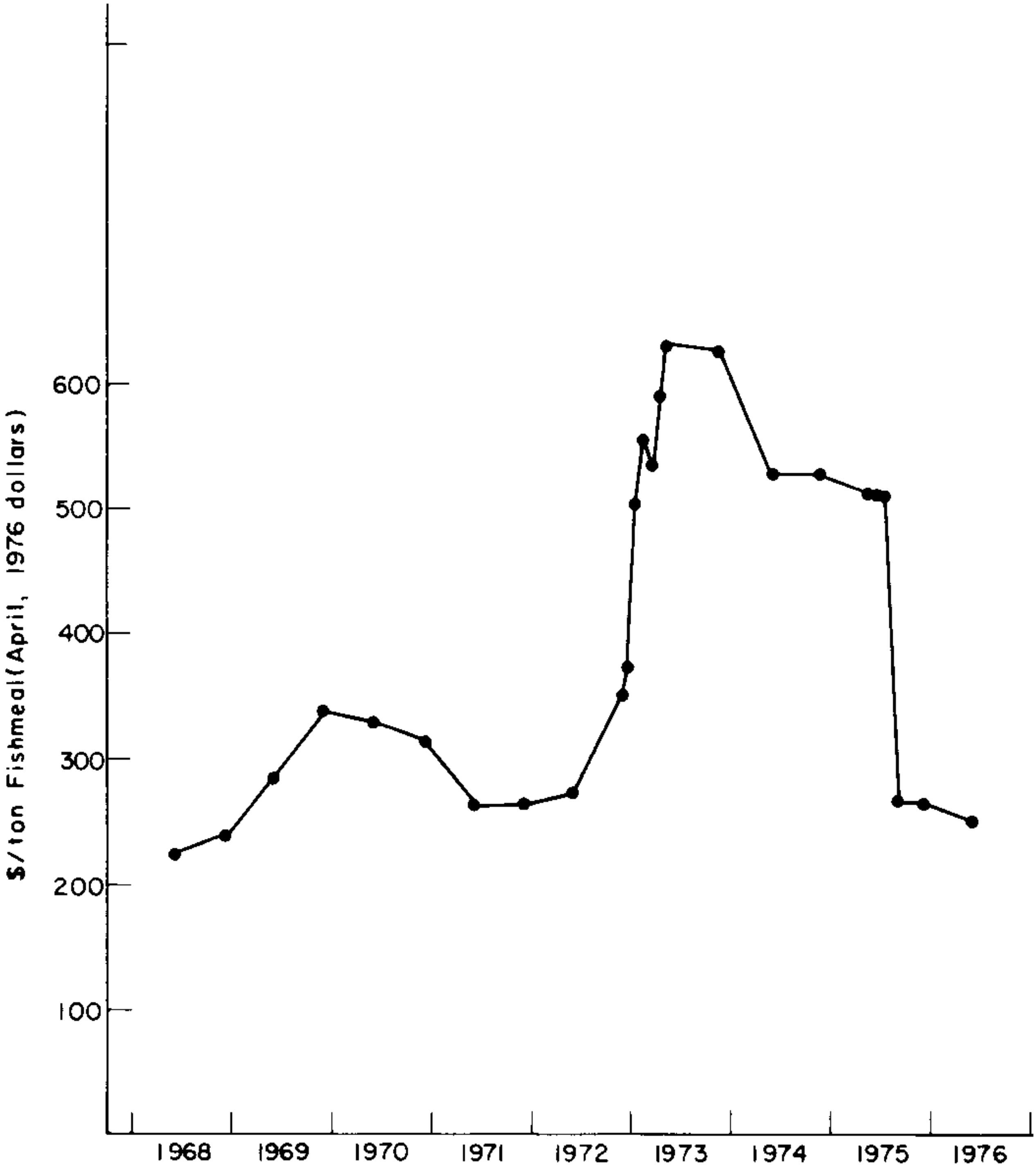

FIGURE 3.2 Fishmeal Price History

To understand the probable costs of labor and fuel for protein drying, it is necessary first to describe the conditions under which the drying is expected to be carried out and the ways in which some specific process variables determine costs.[gg]

Drying a moist (80% water content) high-protein slurry to a salable product (less than about 10% water) is not without difficulties. The operation must be designed to minimize or tolerate the tendencies of the material to foam and stick, and at the same time the protein must not be heated to temperatures at which component amino acids are degraded and nutrient values lost. Many simple types of dryers will run afoul of one or both of these problems. A type of dryer that has found application in the past for drying difficult materials such as beef blood consists of a series of rotating concentric cylindrical drums under moderate heat and partial vacuum within a stationary shell. The design[hh] includes the capability for recycling partially dried material and mixing this with wet material entering the dryer to improve the flow properties of the sticky input.

Dryer capacity and operation is best thought of in terms of units of water removed per given time period. Under conditions that will preserve the nutritional value of the protein,[ii] the smallest economical drying system[jj] (hereafter referred to as the *minimal system*) would remove approximately 1000 lbs of water per hour from the protein product[8]. Given that the feed is 80% water, the total wet weight of feed would be approximately 1250 lbs per hour — the extra 250 lbs being dry weight, of which approximately 66%, 165 lbs, would be actual protein.

Before proceeding, it is instructive to note how sensitive the final output rate (165 lbs of protein per hour, 100% protein basis) of the system is to small changes in the input moisture content. Below are calculations parallel to the one in the previous paragraph based on assumed input water contents of 85% and 75% rather than 80% as above:

	Input Moisture Content = 85%	*Input Moisture Content = 75%*
Input wet feed per hour for 1000 lbs/hr potential water removal	1,176.5 lbs	1,333.3 lbs
Dry content of wet feed/hr (66% protein)	176.5 lbs	333.3 lbs
Output per hour (100% protein basis)	116.5 lbs	220.0 lbs

Clearly, any adjustments that minimize the input water content to the dryer may make an appreciable difference in the costs of drying. Variations in pH, temperature, and other factors in the predrying stages might influence the retention of water, and such manipulations could be usefully explored as operating systems are brought into being. It is also possible that small additions of low-toxicity volatile protein precipitators such as acetone or ethyl alcohol may prove beneficial.[kk] *Modest* additions of salt might also be tried, but limitations on the salt content of the ultimate product will constrain use.

[gg] We are indebted to Mr. R. L. Alwood of Vincent Processes, Inc., Tampa, Florida, for information on dryer operating characteristics and costs.

[hh] For reference, the type of dryer referred to is known as a *stationary shell type vacuo-dehydrator.*[8]

[ii] 135°C product temperature, produced by a furnace operating at 800–1000°C discharging heated air to the dryer at 180°C.

[jj] Smaller systems than the one contemplated could be built, but their capital cost would be no cheaper than the "minimal system."

[kk] Acetone and ethanol are both sufficiently volatile to be efficiently removed in the dryer.

After this long digression, we are now ready to return to the estimation of the operating costs of labor and fuel for drying the protein.

> *Assumption #8: One worker (at a total labor cost of $6.50–9.00/hour) can operate the dryer system*[11] from the screw press through the bagging operation, regardless of the size of the dryer.

Given this labor cost per hour, and the 165 lbs of protein per hour (100% protein basis) output computed earlier, the unit labor cost of drying the protein for a system of minimal size is:

$$\frac{(650\text{–}900¢/\text{hr})}{165\ \text{lbs/hr}} = 3.94\text{–}5.45¢/\text{lb } 100\%\ \text{protein}$$

The operating fuel cost appears to be approximately 1¢/lb of 66% protein product, or about 1.5¢/lb of 100% protein.[8] Given this, we can now compute the operating credit per pound of protein produced for those areas that can use minimal drying systems:

TABLE 3.8

Net Operating Revenue from "Adventitious Protein" For Minimal-System Drying Operations (¢/lb, 100% protein basis)

Revenue from protein sale: 23.3–30¢

LESS:	*South*	*Northeast*	*West*
Cost of acid	1.3¢	1.6¢	2.1¢
Labor for drying	5.5–3.9¢	5.5–3.9¢	5.5–3.9¢
Fuel	1.5¢	1.5¢	1.5¢
Net Credit per pound of protein (100% protein basis)	15.0–23.3¢	14.7–23.0¢	14.2–22.5¢

These data are expressed per pound of protein. To find the operating credit per pound of shell waste residual for entry into Table 3.7, for each of the minimal-system areas low-high estimates have been multiplied by the high-low range of the ratio of

$$\frac{\text{lbs of adventitious protein}}{\text{lbs of shell waste residual}}$$

for that area. To reiterate, all entries in Table 3.7 are expressed in terms of their impact on the ultimate cost of shell waste residual. If there is a 2¢/lb of protein credit and one half pound of protein is made in the process of producing each pound of shell waste residual, the appropriate credit per pound of shell waste residual is 1¢.

For areas that require greater than a minimal drying system, we must make a further adjustment. Because of assumption #8 (a single worker can handle the system regardless of size), the unit drying labor cost for nonminimal systems is decreased by the factor:

$$\frac{1000\ \text{lbs/hour}}{\text{water removal capacity (lbs/hour) for system}}$$

Thus a system with double the minimal water removal rate of 1000 lbs/hour would be expected to operate at half the unit labor cost.

---

[11] The dryer system under consideration consists of a light screw press/conveyor for the input to the dryer, a furnace and dryer combination with a collector for the product, and appropriate exhaust fans and pollution controls, a small grinder, and an automatic bagging system.

Up to this point, we have begged the question of how large a drying system is needed for each of the designated locations of wet waste processing around the country. A proper resolution of this issue would involve a complex optimization — trading off the decreased cost of labor, the value of excess capacity to handle peak seasonal loads, the year-to-year variability in waste available and peak loading, and of course the added cost of raising additional capital. Rather than attempt to construct such an optimization model, we have chosen the following simplifying assumption:

> *Assumption #9: The capacity of the drying system required for each area will be such as to handle all necessary protein and shell waste residual drying*[mm] in 3000 hours of annual operation.[nn]

In other words, the number of pounds per hour of water removal capacity was figured as:

lbs H_2O removal/hr =

$$\frac{\dfrac{\text{lbs protein/year[oo]}}{\text{.165 lbs protein/lb water}} + \dfrac{\text{lbs shell waste residual/yr[pp]}}{\text{.433 lbs shell waste residual/lb water}}}{\text{3000 hours/year operation}}$$

Where the required rate of water evaporation for the protein was below 1000 lbs/hour, it was assumed that the minimal system would be built. After the appropriate adjustment in unit labor costs, the net protein credit for areas with nonminimal drying systems was treated in the same fashion as was described earlier for the minimal systems in order to calculate the entries in Table 3.7.

- Drying of shell waste residual — labor and fuel cost

This cost was computed in similar manner to the costs described above for drying protein. For minimal systems, the computed cost was .8–2.3¢/lb of shell waste residual, and for nonminimal systems with higher rates of water removal the cost was proportionately less.

System-based Cost Estimates For the wet waste-shell waste residual production phase, we have included two kinds of costs in the "system-based" group — depreciation and minimum required return on investment. Both of these are directly related to the capital investment required to begin production.

[mm] One properly designed dryer can handle shell waste residual as well as protein drying. For purposes of estimating the amount of dryer capacity required for shell waste residual, an input moisture content of 50–70% was assumed for the shell waste residual, leading to an output of 433–1000 dry pounds per hour of operation for a minimal-size drying system. This in fact may even be somewhat pessimistic if, as it now appears, the shell waste residual can be safely dried at higher temperatures (faster) than the protein.

[nn] 3000 hours of annual operation would be equivalent to 1½ shifts per day for a five day week for a fifty-week year. In actual practice it can be anticipated that during peak-load portions of the year the system would be required to operate three shifts per day for possibly a six day week. The manufacturer of the dryer[8] advises that the system is sufficiently reliable to be used in this way.

[oo] For each area, this quantity was computed by dividing the total adventitious protein in that area (Table 3.5) by three, in accordance with the assumption that one-third of the waste is directly available to the shellfish processor we are now considering.

[pp] For each area, this quantity was computed by dividing the total shell waste residual producible in that area (Table 3.6) by three, and is shown in the first column of Table 3.7.

For the minimal dryer system our information is that capital costs[4,8] are approximately as follows:

	Thousands of Dollars
Meat/bone separator and associated equipment (e.g., pumps, rotary vacuum filter)	25
Dryer-associated system (furnace, dryer, collector, exhaust fans, screw press conveyor for input to the dryer, bagging system)	67
Miscellaneous	0–20
TOTAL	92–112

It may be noted that we have not made any explicit provision for the cost of floor space or a new building. If the system cannot fit within the existing structure of the large shellfish processing plant, or if existing operations must be moved to a new location to accommodate the space needs of the waste processing units, then some added capital costs should be included in the total required investment.

For nonminimal systems, we have adopted the rule of thumb[8] for estimating capital costs of variously-sized dryer systems that capital cost rises with the two-thirds power of capacity. That is, for our purposes,

$$\frac{\text{capital cost for } y \text{ lbs/hr water removal system}}{\text{capital cost for 1000 lbs/hr water removal system}} = \left(\frac{y}{1000}\right)^{2/3}$$

Calculations indicate that the meat/bone separator of the size we have included in cost estimates to this point has adequate capacity (5000 lbs/hr) for all but the very largest of potential shell waste processing plants; there is little need to include an allowance for additional expenditures on this item.

Given the total capital costs for each area computed in this way, the remaining task for this section is to indicate how these capital expenditures are translated into unit costs for depreciation and return on investment.

- Depreciation

Assumption #10: For investment purposes,[aa] the value of the initial investment may be assumed to decline by 10–20% per year.

- Minimum required return on investment

Assumption #11: The minimum before-tax expected return on investment that would be required to induce a rational firm to make a contemplated investment in shell waste processing is between 20–40% of the total capital investment per year.

The lower value of 20% before-tax annual return on investment is somewhat more than the equivalent of what a corporation (48% federal tax bracket) can realize with relatively low risk from tax-free bonds. Investment floors for some large companies are reported to be approximately 24%.[9]

[aa] The proper assessment of the decline in the value of an investment with time (what may be called *true* depreciation) may be different from the rate of decline in value that may be assumed for tax purposes (*tax-basis* depreciations). Competent legal counsel should be sought in assessing the latter.

The higher value of 40% before-tax annual return on investment was arrived at after consideration of the general riskiness of the scheme. This kind of operation has not yet been proven to be economically feasible in practice. Unforeseen circumstances may cause operating costs to be higher or operating revenues lower than presently estimated. For both the high and low figures, the reader may wish to substitute his/her own judgments as to the minimum return on investment that would be required by a prudent shellfish processor, given the risks and available alternative investments.

To translate the sum of the 10–20% annual depreciation cost and the 20–40% minimum required annual return on investment into unit costs for entry onto Table 3.7, the following procedure was followed:

A) For determining the "low" estimated unit cost of depreciation and minimum return (left-hand entry in Table 3.7),

1. The low value of required investment was determined (either the "minimal system" value of $92,000 or some higher amount as determined by the higher-capacity dryer cost formula shown on p. 41)
2. Minimum unit cost was calculated as

$$\frac{(.10 + .20)\ (\text{low value of required investment})}{\text{high value of lbs shell waste residual product}}$$

B) For determining the "high" estimated unit cost of depreciation and minimum return per year (right-hand entry in Table 3.7)

1. The high value of required investment was determined (either the "minimal system" value of $112,000 or some higher amount as determined by the higher-capacity dryer cost formula shown on p. 41)
2. Maximum unit cost was calculated as

$$\frac{(.20 + .40)\ (\text{high value of required investment})}{\text{low value of lbs shell waste residual product/yr}}$$

Comment on the Results in Table 3.7 The final two columns in Table 3.7 give the answers we have been working toward. The first, "Total Cost, ¢/lb Shell Waste Residual" gives the summation of the earlier columns and represents the estimated ranges of the long-run market price that would be needed to induce a rational shellfish processor in each area to institute production. The final column of Table 3.7 makes use of the data given in Table 3.6, on the percentage of chitin content expected for the shell waste residual in each area, to recompute the results given in the earlier column on the basis of the ¢/lb. price of the chitin content *in* the shell waste residual required to justify investment. This is a more likely basis for the ultimate price determination for this material although, as will be apparent in Section 3.1.5 below, there may also be reason for some negative price adjustment on the basis of calcium carbonate content.

It should be noted that many of the numbers on the left-hand (optimistic) side of the last columns of Table 3.7 are enclosed in parentheses, indicating negative numbers. For those areas (Maine, Maryland/Delaware, Virginia, North Carolina, South Carolina, Georgia, Flordia W #2, Alabama/Mississippi/Florida, Louisiana #1, Louisiana #2, Texas #1, Oregon/Washington, and Washington), the apparent result is therefore that, at least under the most optimistic set of assumptions we have used, a shellfish processor holding at least one-third of the waste available in the area may be able to earn a sufficient rate of return on the protein alone to justify the required investment without any need for revenue from the sale of shell waste residual. On the other hand, the results in the right-hand (pessimistic) side of the same column indicate that although there may be no areas where the protein production can pay on its own, there are a number of areas (Maryland/Delaware, Virginia, North Carolina, Georgia, Florida W #2, Alabama/Mississippi/Florida, Louisiana #1, and Louisiana #2) where the minimum required return on investment would be earned with shell waste residual prices of less than fifteen cents per pound.

The data in Table 3.7 are in terms of unit costs and credits. Total annual cash flow information can easily be computed by multiplying the unit costs and credits by the total production quantities given in the first column of Table 3.7. For example, for Louisiana #1 producing .902–1.688 million pounds of shell waste residual per year, there would be the following annual costs and credits:

	Low Cost Estimate, ¢/lb Multiplied by "Optimistic" Quantity, 1.688 million lbs shell waste residual	*High Cost Estimate, ¢/lb Multiplied by "Pessimistic" Quantity, .902 million lbs shell waste residual*
Cost of labor for protein separation, less disposal credit, 2.0–3.7¢/lb.	$33,760/yr.	$33,374/yr.
Credit for protein sale less labor and fuel for protein drying, (11.0–5.7¢/lb.)	($185,680/yr.)	($51,414/yr.)
Shell waste residual drying: labor and fuel, .3–1.2¢/lb.	$5,064/yr.	$10,824/yr.
10–20% depreciation + 20–40% return on capital investment, 3.2–11.5¢/lb.	$54,016/yr.[rr]	$103,730/yr.[ss]
Total cost (profit) exclusive of revenue from sale of shell waste residual, (5.5)–10.7¢/lb.	($92,840/yr.)	$96,514/yr.

3.1.4.2 Production Costs for the Additional Shell Waste Residual That Might be Produced from Purchased and Transported Wet Waste In Assumption #5 (p. 32 above) it was assumed that the two-thirds of each area's waste that was *not* immediately available on site to our hypothetical large shellfish processor could be procured at the cost of transport plus $0–20/ton purchase cost. In this part we examine the *incremental* costs[tt] required for the large shellfish processor considered in the previous part to expand its planned production by bringing in the full quantity of waste available from its local fifty-mile-radius area. Among other objectives, in this way we shall attempt to get an indication from each area as to whether it might be desirable for the waste processor to institute at the start a system for transporting wet waste from neighboring plants.

Table 3.9 shows the resulting series of estimates. Below we shall discuss our assumptions

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[rr] Based on investment of $\frac{\$54,016}{.1 + .2} = \$180,053$

[ss] Based on investment of $\frac{\$103,730}{.2 + .4} = \$172,883$

[tt] It may be helpful to give a concrete example to illustrate the notion of *incremental* costs. Assume that a shellfish processor has the capability with a minimal system of making shell waste residual from his own waste at a total cost of 20¢/lb, but that at the rate at which production would occur, even the minimal system would be utilized to less than one-third of its full capacity. Consider further, that the full quantity of waste available from other shellfish processors in the area (twice the original production amount) could be purchased, transported, and processed with total process-based costs of 10¢/lb. In this example, there would be no additional capital expenditure required (because the minimal system contemplated to handle the original load could handle the three-fold larger load without expansion) and hence no additional system-based costs. The total incremental costs of producing the additional 2/3 of the waste available in this hypothetical area would be 10¢/lb, although average costs for the total production would be: (1/3)(20¢/lb) + (2/3)(10¢/lb) = 13.3¢/lb

and calculation procedures for this table on a column-by-column basis, wherever there is a notable difference from the assumptions and procedures followed for the corresponding column in Table 3.7 (p. 35).

Process-based Cost Estimates

- Purchase of wet waste, and cost of labor for protein separation

For the category of costs in Table 3.7 connected with purchase of wet waste, and cost of labor for protein separation, there was assumed to be a $5/ton wet waste credit for savings of alternative disposal costs. Instead of this credit, we now have a $0–20/ton (0–1¢/lb) wet waste purchase cost.[uu] The assumption for the cost of labor for protein separation (.39–.54¢/lb of wet waste) is unchanged. Combining both costs, the entries for Table 3.9 were therefore computed as:

$$\frac{\text{(.39–1.54¢/lb wet waste)(\# lbs wet waste available in area)}}{\text{(\# lbs shell waste residual producible in area)}}$$

- Transport costs

This is a very difficult category of costs to estimate with any assurance of accuracy. The calculation after Assumption #11 is an attempt to gauge transport costs for a set of conditions that is reasonably representative of national average conditions. However, the detailed geographic arrangement of wet waste sources in different areas, local labor practices, and other factors may give rise to substantially different transport costs for specific areas of the country than predicted by our model. Assumption #11 covers the composition and costs of the trucking unit and Assumption #12 covers the dynamics of the trucking operation and the geographic distribution of wet waste sources.

> *Assumption #11: Wet waste will be transported in containers in standard leased rack-body trucks, with a load space of approximately 18′ × 7′–8′ × 4′.*[vv] *Two workers will operate the truck.*[ww] *Costs for operation of each trucking unit of one truck and two workers covering 50,000 miles in the course of each year (200 miles per day) are approximately*

Item		
Truck Rental:[xx]		
($125/week) × 50 weeks	=	*6,500*
+($.06/mile) × 50,000 miles	=	*3,000*
Gas $\frac{\text{(50,000 miles)(60¢/gal)}}{\text{5–10 miles/gal}}$	=	*3,000– 6,000*
Total labor cost for two workers	=	*26,000–36,000*
(@ $13–18,000 each)		*$38,500–52,500*

[uu] In some cases it has been reported to us that prices as high as $65/ton have been paid for wet shrimp waste. However, we have chosen the $20/ton figure as our high estimate because we believe that this may be near the highest level likely to be conducive to long-run cooperative relationships between waste suppliers and waste processors. $20/ton (1¢/lb) of wet waste translates ultimately into approximately a 20¢/lb contribution to the ultimate cost of chitin, given that the chitin content of wet waste is about 5%.

[vv] Given that shrimp waste apparently weighs about 13 lbs/cubic foot, the capacity of the truck is approximately 7,500 lbs of waste. For purposes of computation we shall assume that crab waste has equivalent density and involves identical trucking expenses.

[ww] Two workers per truck is the current practice for an existing crab waste trucking operation in Hampton, Virginia.

[xx] Truck dimensions and leasing costs were supplied by a Boston truck rental firm.

TABLE 3.9

Incremental Costs of Additional Shell Waste Residual Which Could be Produced from Purchased and Transported Wet Waste (Assumed to be 2/3 of Waste Potentially Available in Each Area)

		Costs in ¢/lb Shell Waste Residual						
Area	*Quantity of Additional Shell Waste Residual Lbs × 10⁶*	*Purchase of Wet Waste ($0–20/Ton of Waste) & Cost of Labor for Protein Sep.**	*Transport Hi Q* Lo Q**	*Credit for Protein Sale Less Labor and Fuel Cost for Protein Drying***	*Shell Waste Residual Drying: Labor and Fuel**	*10–20% Depreciation + 20–40% Return on Added Capital Investment**	*Total Cost ¢/lb Shell Waste Residual**	*Total Cost ¢/lb Chitin in Shell Waste Residual**
Maine	.605–1.082	3.7–14.6	7.1–17.0	(12.4–7.1)‡	.1–1.1	2.4–6.5	0.9 –32	2.6 –108
Massachusetts	.207– .355	3.3–12.9	10.9–24.9	(10.0–5.5)	.8–2.3	0 –0	5.0 –35	15.4 –127
Md./Del.	2.492–3.244	1.4– 5.4	2.4– 4.1	(10.9–4.7)	.1– .2	1.7–4.4	(5.3)– 9.4	(26) – 54
Virginia	2.939–3.831	1.4– 5.4	3.0– 3.5	(10.9–4.7)	.1– .2	1.6–4.2	(4.8)– 8.6	(23) – 50
N. Carolina	2.151–2.839	1.4– 5.7	2.7– 4.8	(11.1–4.9)	.1– .2	1.8–4.8	(5.1)–10.6	(24) – 60
S. Carolina	.518– .719	2.0– 7.7	5.4– 9.9	(11.1–4.5)	.3–1.5	1.6–2.3	(1.8)–16.9	(7.4)– 87
Georgia	1.821–2.401	1.6– 6.3	3.2– 5.7	(10.4–4.6)	.1– .2	1.9–5.0	(3.6)–12.6	(15.5)– 66
Florida E#1	.246– .523	2.3– 9.1	7.4–20.9	(9.6–3.9)	.6–2.3	.7–0	1.4 –28	6.3 –161
Florida E#2	.201– .259	1.9– 7.4	14.8–25.7	(9.2–4.3)	.8–2.3	0 –0	8.3 –31	30 –131
Florida Keys	.184– .262	4.1–16.2	14.7–28.0	(11.1–6.2)	.8–1.9	0 –0	8.5 –40	26 –139
Florida W#1	.476– .611	1.9– 7.5	6.3–10.8	(10.0–4.7)	.5–2.3	1.2–1.3	(0.1)–17.2	(1.4)– 72
Florida W#2	.855–1.309	1.9– 7.4	5.9–12.0	(11.3–5.3)	.1– .4	2.2–5.2	(1.2)–19.7	(4.2)– 88
Ala./Miss./Fla.	1.057–1.764	2.1– 8.2	4.4– 9.7	(11.7–5.7)	.1– .2	2.1–6.9	(3.0)–19.3	(10) – 89
Louisiana #1	1.805–3.375	2.6–10.2	3.4– 5.7	(11.9–6.5)	.1– .2	1.7–6.2	(4.1)–15.8	(13.4)– 65
Louisiana #2	.927–1.347	1.7– 6.6	5.7–11.1	(11.6–4.8)	.1– .3	2.3–5.4	(1.8)–18.6	(7.3)– 98
Texas #1	.787–1.026	1.8– 7.2	7.5– 6.5	(11.2–4.9)	.1– .7	2.1–4.5	0.3 –14	1.2 – 66
Texas #2	.483– .631	2.2– 8.8	6.1–10.7	(10.5–4.8)	.4–1.7	1.3–1.8	(0.5)–18.2	(1.7)– 73
Texas #3	.251– .327	3.1–12.3	1.8–20.5	(9.7–5.8)	.8–2.3	0 –0	6.0 –29.3	16.8 – 84
California #1	.359– .651	3.8–14.9	1.8–14.4	(11.3–6.2)	.3–1.7	1.6–2.5	6.2 –27.3	18.2 – 88
California #2	.386– .582	2.1– 8.3	6.9-13.3	(10.0–4.0)	.5–2.3	1.0–0	0.5 –19.9	1.9 – 96
California #3	.173– .244	1.9– 7.5	5.8-29.8	(9.2–3.8)	.8–2.3	0 –0	9.3 –36	36 –181
Oregon/Wash.	.471– .937	3.0–12.0	8.2–10.9	(11.4–4.9)	.1– .9	2.1–5.9	2.0 –25	6.7 –114
Washington	.741–1.087	2.1– 8.3	7.1–13.9	(11.2–4.8)	.1– .6	2.2–5.0	0.3 –23	1.1 –111
Alaska (whole state)	N.A.							

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*For each column, the number or the left represents the cost resulting from the most optimistic highest quantity and lowest cost assumptions, and the number on the right represents the cost resulting from the most pessimistic assumptions.

‡Numbers in parentheses are negative costs (credits)

**Revenue from protein sales minus labor, acid, and fuel to run the equipment. The left number in each entry results from assuming a protein price of 30¢/lb. of 100% protein and optimistically low operating production costs (see text). The right number in each entry results from assuming a protein price of 23.3¢/lb. of 100% protein and pessimistically high operating production costs. (See text).

***Assuming three person hours per hour of operation ($6.50–9.00 cost per person-hour) processing 5,000 lbs of wet waste per hour = .39–.54¢/lb of wet waste processed. Deducting $5/ton (.25¢/lb) disposal credit, net cost through the separation step is .14–.29¢/lb of wet waste.

The bottom line, total annual cost per trucking unit shown above tells us part of what must be known to assess trucking costs per unit of shell waste residual produced from the trucked material. The other part is some determination of how much waste would be brought in by each trucking unit, given that a full load is about 7,500 lbs and that the truck cannot be expected to travel more than about 200 miles per day.

Assumption #12: To avoid excessive spoilage of the waste, the trucking schedule must be designed so that each location at which shell waste is gathered is visited by a collection truck at least once each working day. For ease of modelling transport flows, sources of shell waste are assumed to be arranged evenly along a linear coastline extending fifty miles in both directions from the waste processing center.

Given this assumption, the maximum one-truck operation would make two 100-mile round trips each day — one extending to the fifty-mile limit and back in each direction. Thus two full loads of waste would enter the plant per day or, on an annual basis approximately[yy]

$$(2 \text{ loads/day})(7{,}500 \text{ lbs/load})(250 \text{ days/year}) = 3.75 \times 10^6 \text{ lbs/year}$$

For all areas in which the quantity of wet waste to be trucked is less than this amount we assume that costs are those listed for one trucking unit in Assumption #11, or, in terms of ¢/lb wet waste delivered,

$$\text{transport cost (¢/lb wet waste)} = \frac{(\$3.85\text{–}5.15 \times 10^4)(100¢/\$)}{\text{annual \# lbs waste carried}}$$

millions of lbs wet waste carried per year	*¢/lb wet waste transport cost*	*$/ton wet waste transport cost*
1	3.85–5.15	77–103
2	1.93–2.58	38.5–51.5
3	1.28–1.72	25.5–34.5
3.75	1.03–1.37	20.5–26.5

Unit costs are expected to rise dramatically if the truck must be operated at substantially under its capacity.

For areas in which the waste to be trucked is greater than 3.75 million pounds per year, at least two trucks must be used. However, when one uses assumption #12 to calculate the maximum quantity of wet waste that could be delivered by a two-truck operation there is a surprising result: two trucks would have an effective delivery capacity three times that of one truck (11.25×10^6 lbs). This is because each truck could make three round trips per day, collecting over 16.7-mile intervals, from 1) the farthest 50-mile-distant point to a point 33.3 miles distant, thence returning directly to the plant (100 miles round trip); 2) a point 33.3 miles distant to a point 16.7 miles distant (67 miles round trip); 3) a point 16.7 miles distant to the waste processing center (33 miles round trip), still staying within the 200 miles maximum travel for each truck while visiting each waste pick-up point once each day. By similar arrangement of routes, it can be shown that the capacity of a three-truck operation would be five times the capacity of a one-truck operation (18.75×10^6lbs). Transport cases were calculated in parallel with the calculation shown for the one-truck situation except that the total cost shown in the numerator of the equation was multiplied by the number of trucks required.

[yy] This calculation assumes a 250-day year. If the seasonality of waste generation does not permit collection of waste for this many days per year the effective capacity of each trucking unit will be somewhat less — although it is possible that some savings in annual costs may be possible if the truck lease can be obtained on less than a yearly basis and if other ways can be found to use the labor of the trucker/loaders.

After computation of the transport costs in ¢/lb wet waste, the entries for Table 3.9 were calculated simply as

¢/lb shell waste residual cost due to wet waste transport =

$$\frac{(\text{¢/lb wet waste})\ (\text{\#lbs shell waste residual})}{(\text{\#lbs wet waste})}$$

- Credit for protein sale, less labor and fuel for protein drying
- Cost of drying shell waste residual

These costs were computed similarly to the costs in the corresponding columns of Table 3.7, except for a downward adjustment of unit labor costs if increased protein and shell waste residual production would require the installation of larger-capacity dryers.

Because Table 3.9 is constructed in terms of incremental costs and revenues (see note, p. 45), the entries to these columns reflect not only the decreased cost of drying the protein and shell waste residual from the two-thirds of each area's waste that is purchased and transported, but also the additional cost savings on the original one-third of each area's waste that was covered in Table 3.7.

System-based Cost Estimates The capital costs of the larger drying system needed in the various areas to handle the increased production was calculated according to the formula given on page 42. The capital costs for the smaller system were then subtracted from the capital costs for the larger system to obtain the increment in capital costs required.[zz] These estimates were then divided by the increase in the quantity of shell waste residual production to obtain the incremental capital costs per annual pound of shell waste residual production, and the allocation for depreciation and minimum required return on investment was calculated (as before) as 30–60% of the capital expenditure per annual pound of shell waste residual production.

Comment on the Results in Table 3.9 Comparing the results in Table 3.9 with those in Table 3.7, it can be seen that for some areas the shell waste residual production costs are smaller with the inclusion of the purchased and transported wet waste, and for some areas the shell waste residual production costs are larger with the inclusion of the additional material. The areas for which production costs are smaller in Table 3.9 than in Table 3.7 are predominantly those areas with relatively small amounts of waste available.[aaa] For these plants, the advantages of fuller utilization of the drying systems and (for those that must build some additional drying capacity) lower unit labor costs for the drying operations more than compensate for the costs of purchase and transport of wet waste. On the other hand, for areas in which large enough quantities of waste may be available to achieve nearly full utilization of a minimal drying system without the importation of waste by truck, shell waste residual produced from purchased and transported wet waste would raise average production costs.[bbb] However, it should also be noted that most of these plants[ccc] still show negative numbers for the estimated total cost of shell waste residual under the optimistic (left-hand side of the column) set of assumptions. This means that for plants in these areas, revenue from the sale of protein alone may provide sufficient return to justify the investment in added capacity to handle the purchased and transported wet waste.

[zz] Entries of zero in this column indicate that a minimal-size dryer system would be able to handle all the waste available in the area (see note, Table 3.9).

[aaa] Massachusetts, South Carolina, Florida plants E#1, E#2, Keys, and W#1, Texas #1$_{\text{high cost}}$, Texas #2, Texas #3, Calif. #1$_{\text{high cost}}$, Calif. #2, Calif. #3, and Oregon/Washington$_{\text{high cost}}$.

[bbb] Areas where this occurs are Maine, Md./Del., Virginia, N. Carolina, Georgia, Florida W#2, Ala/Miss/Fla, Louisiana #1, Louisiana #2, Texas #1$_{\text{low cost}}$, Oregon/Wash$_{\text{low cost}}$, and Washington.

[ccc] Md./Del., Virginia, N. Carolina, Georgia, Fla. W#2, Ala/Miss/Fla, Louisiana #1, Louisiana #2.

Theoretically, shell waste processors in any of the areas could operate satisfactorily with or without a collection system to gather additional raw material from neighboring shellfish processing plants. However, to simplify further analysis, it is reasonable to make the following assumption:

> *Assumption #13: Processors will not choose the option of opening 1/3-production plants (based only on their own waste but not importing waste from neighbors) if either of the following circumstances apply:*
>
> *1) Average production costs for shell waste residual would be lower for a full-production plant than for a 1/3-production plant, or*
>
> *2) A full-production plant could earn the minimum required return on investment from the sale of protein alone.*

For further analysis of cases in which the one-third production option is assumed not to be preferred, the weighted average shell waste residual production costs of the full-production plant are calculated as described in the note on page 45.

3.1.5 Costs of Producing Chitosan From Shell Waste Residual

The previous section developed estimates of the minimum prices that would have to be obtained for shell waste residual to induce rational shellfish processors to institute production in different areas of the country. By contrast, in this section the focus shifts from the shellfish processor to the prospective purchaser of the shell waste residual — the firm that will make and sell chitosan. The question addressed is, "What price of the final chitosan product would allow a chitosan producer to pay the prices necessary to support production of various quantities of shell waste residual in different areas?"

In a procedure similar to that for the previous section, the cost estimates will be divided into two categories:

- *Process-based cost estimates* in this case include purchase and rail transport of shell waste residual to a national chitosan manufacturing plant, cost of hydrochloric acid for demineralization[ddd] ,and the cost of caustic soda for deacetylation[eee].
- *System-based cost estimates* in this case were made for general labor requirements, utilities, amortization of capital equipment and structures, and minimum required return on investment.

Labor costs have been estimated on a system-requirement basis for this section because detailed information is not available on the labor and power inputs for individual process steps.

For purposes of analysis it is helpful to make a further subcategorization of the process-based cost estimates. The minimum cost of shell waste residual, rail transport cost, and the cost of hydrochloric acid for demineralization all differ for various sources of shell waste residual and will influence the choice of which material will be purchased for chitosan manufacture. By focussing on these three costs, it will be possible to arrange the shell waste residual sources in order of likely preference from the chitosan manufacturer's point of view.

> *Assumption #14: The chitosan manufacturer will purchase shell waste residual from those sources which allow the production of chitosan at minimum unit cost.*

[ddd] *Demineralization* is the removal of $CaCO_3$ from the shell matrix.

[eee] Deacetylation is the step in which chitosan is produced from chitin by removal of the acetyl groups under strongly alkaline conditions.

3.1.5.1 Costs Which Vary with the Source of Shell Waste Residual Tables 3.10 and 3.11 summarize this set of costs for the different sources of shell waste residual production. Table 3.10 is based on the most optimistic set of cost and quantity assumptions—including the shell waste residual cost estimates on the left-hand side of the column in Tables 3.7 and 3.9. Conversely, Table 3.11 is based on the most pessimistic set of cost and quantity assumptions—including the shell waste residual cost estimates on the right-hand side of the columns in Tables 3.7 and 3.9.

Purchase of shell waste residual In both Tables 3.10 and 3.11 the first four columns express costs in terms of ¢/lb of ultimate chitos*an* product. This measure differs from the measure used in the final column of Tables 3.7 and 3.9, "¢/lb chit*in* in shell waste residual" because chitin loses weight on deacetylation to chitosan. From the chemistry of this process, the theroretical yield is one lb of chitosan from 1.26 lbs of chitin.[fff]

For Table 3.10, we were faced with the difficult problem of assessing the likely minimum selling price of shell waste residual for those areas in which, under the optimistic set of assumptions, production would be justified by the protein revenue alone, with little or no need for subsidization from the sale of shell waste residual. A low but arbitrary minimum selling price was chosen for these producers—4¢/lb of chitin content, or 5¢/lb of chitosan ultimately produced—which should amply cover the cost of drying the shell waste residual and preparing it for shipment. As will be seen later, if the shell waste residual market behaves according to traditional economic theory, the actual selling price for all producers will depend on the price needed to bring the most marginal economic producer into the market to supply the final marginally-justified quantity of shell waste residual.

Transportation of shell waste residual to the site of chitosan production Freight rates are determined in a complex manner according to the type of commodity hauled, the peculiarities of local routing rules between the origin and destination of the cargo, and other factors. Conversations with a railroad company and a chemical supplier indicated that it was not possible to predict simply and reliably the probable freight charges between arbitrarily-selected points in the country.

Recognizing the true complexity of freight-rate determinations and the uncertainty in attempting to create a simple formula to represent them, in this study we must nonetheless make some approximate determination of reasonable charges for shipping shell waste residual from different areas to a chitosan production facility. Data in a standard statistical reference[10] indicate that, for the most recent years available (1971–3), the average rail shipping cost per ton-mile for all commodities was approximately 1.6¢. We suspect that average costs are somewhat higher now than they were in 1971–3, and that costs for shipping a light, bulky commodity like shell waste residual may be higher than for shipment of average commodities. The transport costs presented in Tables 3.10 and 3.11 are based on the following assumption:

> *Assumption #15: The least expensive form of transportation for shell waste residual will be by rail, at a cost of between 2–3¢/ton-mile, as measured to a chitosan processing facility located in Augusta, Georgia.*

The Augusta, Georgia, location was postulated for the purposes of these calculations because: (1) it is approximately centrally located between major sites of shellfish processing in the Chesapeake, South Atlantic, and Gulf states, and (2) there is a major chlorine/caustic soda producer located in the city, and therefore delivered prices of hydrochloric acid and caustic soda may be lower than elsewhere.

[fff] This theoretical yield is based on the conversion of 100% acetylated chitin to 100% deacetylated chitosan. In actual practice, the chitin will already contain a small percentage of deacetylated amino groups in the crab and shrimp shells, and the deacetylation percentage achieved in the end can be expected to be only about 80–90%. Both of these factors will tend to decrease the amount of chitin needed to produce a pound of chitosan. On the other hand, there has been no provision elsewhere in the analysis for possible losses of chitin in processing. For purposes of estimation, we have assumed that these two sources of error cancel.

TABLE 3.10

Chitosan Production Costs Which Vary with the Source of Shell Waste Residual

High Quantity, Low Cost Assumptions

	Costs—¢/lb Chitosan Produced				*Quantity of Potential Chitosan Production (Millions of Lbs)*	
Source Area of Shell Waste Residual and Level of Production	*Purchase of Shell Waste Residual (Minimum with Low Assumption)*	*Transportation of Shell Waste Residual (to Augusta, Ga.)*	*Acid Demineralization Cost*	*Sum of Costs Which Vary with Source of Shell Waste Residual*	*From Waste in Each Individual Area*	*Cumulative Quantity Within Indicated Costs*
Maine$_{1/3}$**	~5*	3.6	14.1	23	.14	.14
Maine$_{2/3}$	~5*	3.6	14.1	23	.29	.43
Louisiana #1$_{ALL}$	~5*	2.3	17.4	25	1.20	1.63
California #1$_{1/3}$	~5*	7.5	13.9	26	.09	1.72
Florida W#2	~5*	1.3	20	26	.42	2.14
Ala/Miss/Fla$_{ALL}$	~5*	1.8	19.8	27	.57	2.71
Massachusetts$_{1/3}$	9.1	3.5	15.4	28	.04	2.75
Florida W#1$_{ALL}$	~5*	1.5	21	28	.19	2.94
Texas #2$_{ALL}$	~5*	4.1	19.6	29	.20	3.14
S. Carolina$_{ALL}$	~5*	0.7	26	32	.19	3.33
Oregon/Wash$_{1/3}$	~5*	9.9	18.4	33	.10	3.43
Texas #1$_{1/3}$	~5*	4.2	24	33	.10	3.53
Texas #1$_{2/3}$	~5*	4.2	24	33	.20	3.73
Georgia$_{ALL}$	~5*	0.7	28	34	.63	4.36
Louisiana #2$_{ALL}$	~5*	3.3	26	34	.38	4.74
California #2$_{ALL}$	~5*	10.3	22	37	.17	4.91
Oregon/Wash$_{2/3}$	8.4	9.9	18.4	37	.20	5.11
Massachusetts$_{2/3}$	19.4	3.5	15.4	38	.09	5.20
Washington$_{1/3}$	~5*	10.7	22	38	.11	5.31
Washington$_{2/3}$	~5*	10.7	22	38	.22	5.53
N. Carolina$_{ALL}$	~5*	2.1	32	39	.70	6.23
Virginia$_{ALL}$	~5*	2.6	33	41	.91	7.14
Md/Del$_{ALL}$	~5*	3.0	33	41	.77	7.91
Texas #3$_{ALL}$	25	3.8	13.1	42	.14	8.05
Florida E#1$_{ALL}$	10.6	1.7	30	42	.13	8.18
California #1$_{2/3}$	23	7.5	13.9	44	.17	8.35
Florida Keys$_{ALL}$	38	2.2	15	55	.10	8.45
Florida E#2$_{ALL}$	47	2.1	21	70	.08	8.53
California #3$_{ALL}$	54	11.4	24	89	.07	8.60

*A nominal minimum price of 4¢/Lb of Chitin content has been assumed for plants which are profitable even if the shell waste residual were to be discarded, and for plants where the needed revenue from shell waste residual could be less than 4¢/lb chitin content.

**Italics indicate the sources where a shell waste processing protein production facility appears to be sufficiently profitable to warrant investment without any additional income from sale or shell waste residual (under the optimistic set of assumptions).

The subscripts indicate the level of production. The subscript "1/3" indicates that the costs and quantity are based on 1/3 of each area's potential production under the conditions stated for Table 3.7. The subscript "2/3" indicates that the costs are the incremental costs for the additional 2/3 of the area's potential production which depends on purchased and transported wet waste. The subscript "All" indicates that the costs are a weighted average of costs for 1/3 and 2/3 production, where the 1/3-production option is deemed unlikely (see assumption #13).

Table 3.11
Chitosan Production Costs Which Vary with the Source of Shell Waste Residual
Low Quantity, High Cost Assumptions

	Costs—¢/lb Chitosan Produced				Quantity of Potential Chitosan Production (Millions of Lbs)	
Source Area of Shell Waste Residual and Production	Purchase of Shell Waste Residual (Minimum with Low Assumptions)	Transportation of Shell Waste Residual (to Augusta, Ga.)	Acid Demineralization Cost	Sum of Costs Which Vary with Source of Shell Waste Residual	From Waste in Each Individual Area	Cumulative Quantity Within Indicated Costs
Virginia$_{1/3}$	40	4.6	40	84	.21	.21
Louisiana #1$_{1/3}$	57	4.3	25	86	.18	.39
Georgia$_{1/3}$	54	1.3	35	90	.14	.53
Md/Del$_{1/3}$	45	5.5	40	90	.18	.71
N. Carolina$_{1/3}$	50	3.8	39	93	.16	.87
Ala/Miss/Fla$_{1/3}$	69	3.5	29	101	.10	.97
Maine$_{1/3}$	83	6.1	17.1	106	.07	1.04
Virginia$_{2/3}$	63	4.6	40	108	.42	1.46
Florida W#2$_{1/3}$	79	2.6	28	110	.08	1.54
Md/Del$_{2/3}$	68	5.5	40	113	.36	1.90
Texas #2$_{\mathrm{ALL}}$	85	7.3	24	116	.15	2.05
Georgia$_{2/3}$	83	1.3	35	119	.29	2.34
Texas #1$_{\mathrm{ALL}}$	88	7.7	31	126	.21	2.55
Florida W#1$_{\mathrm{ALL}}$	108	2.6	26	137	.14	2.69
Florida W#2$_{2/3}$	111	2.6	28	142	.16	2.85
Ala/Miss/Fla$_{2/3}$	112	3.5	29	144	.19	3.04
N. Carolina$_{2/3}$	107	3.8	39	149	.32	3.36
California$_{\mathrm{ALL}}$	123	12.7	16.5	152	.13	3.49
Texas #3$_{\mathrm{ALL}}$	135	5.9	13.7	155	.10	3.59
Maine$_{2/3}$	136	6.1	17.1	159	.14	3.73
Washington$_{1/3}$	110	21	31	162	.06	3.79
Louisiana #2$_{2/3}$	123	6.5	35	164	.15	3.94
S. Carolina$_{\mathrm{ALL}}$	130	1.3	34	106	.13	4.07
Washington$_{2/3}$	140	21	31	192	.13	4.20
Oregon/Wash$_{\mathrm{ALL}}$	151	20	29	200	.17	4.37
California #2$_{\mathrm{ALL}}$	151	20	31	202	.10	4.47
Massachusetts$_{\mathrm{ALL}}$	207	6.3	20	233	.07	4.54
Florida Keys$_{\mathrm{ALL}}$	223	3.7	18.3	245	.06	4.60
Florida E#2$_{\mathrm{ALL}}$	229	3.7	27	259	.06	4.66
Florida E#1$_{\mathrm{ALL}}$	263	3.2	38	304	.09	4.75
California #3$_{\mathrm{ALL}}$	316	22	−3	371	.04	4.79

*The subscripts indicate the level of production. The subscript "1/3" indicates that the costs and quantity are based on 1/3 of each area's potential production under the conditions stated for Table 3.7. The subscript "2/3" indicates that the costs are the incremental costs for the additional 2/3 of the area's potential production which depends on purchased and transported wet waste. The subscript "All" indicates that the costs are a weighted average of costs for 1/3 and 2/3 production, where the 1/3 production option is deemed unlikely (see assumption #113).

Given this assumption, the entries for Tables 3.10 and 3.11 were calculated using the following formula:

shell waste residual transport cost (\$/lb chitosan) =

$$\frac{(2\text{–}3¢\text{/ton-mile})(\#\text{ lbs shell waste residual})(\#\text{miles to Augusta})}{(2000\text{ lbs/ton})(\#\text{ lbs chitosan})}$$

where $$\frac{\#\text{ lbs shell waste residual}}{\#\text{ lbs chitosan}} = \frac{1.26\text{ lbs chitin/lb chitosan}}{(\text{lbs chitin/lb shell waste residual})}$$

The denominator of the resulting formula is simply the chitin content of the shell waste residual produced in each area, which was given in Table 3.6, p. 33.

Cost of hydrochloric acid for demineralization The chemical reaction that is responsible for dissolving calcium carbonate ($CaCO_3$) from the shell matrix is:

$$2HCl + CaCO_3 = CO_2 + H_2O + Ca^{++} + 2Cl^-$$

Chemical equivalence therefore requires two moles of hydrochloric acid per mole of calcium carbonate removed. Since commercial concentrated HCl is about 12 moles/liter and weighs about 1.18 kg/liter the minimum HCl requirement is 1/6 liter per mole of $CaCO_3$, or:

$$\frac{(1/6\text{th liter HCl})(1.18\text{ kg HCl/liter})}{(100\text{ g }CaCO_3\text{/mole})(.001\text{ Kg/g})} = \frac{1.965\text{ lbs concentrated HCl}}{\text{lb }CaCO_3\text{ removed}}$$

It is not clear exactly how much more than this minimum might be used to perform the demineralization in actual practice. Actual acid use may depend on the desired speed of the reactions, the efficiency with which any excess acid can be recycled, and the quantity of acid that is neutralized or absorbed by other constituents of the shell waste residual (protein and chitin). These questions should be explored in future applied research. For purposes of this study, the following assumption has been used:

> *Assumption #16: The demineralization step requires twice as much hydrochloric acid as would be expected from theoretical chemical equivalence — 3.93 lbs HCl/lb $CaCO_3$.*

Under this assumption, and assuming a favorable delivered price of \$40/ton (2¢/lb) for HCl, the entries for Tables 3.10 and 3.11 were calculated by:

$$\text{demineralization cost (¢/lb chitosan)} = 2¢(3.93)(\text{low-high ratio of } \frac{\text{lbs }CaCO_3}{\text{lb chitin}}\ (1.26)$$

The optimistic-pessimistic range in the ratio of calcium carbonate to chitin for the shell waste residual from each area was determined from the data in Table 3.6 p. 33. This ratio is a crucial parameter. Because shell waste residual made from crab shell will have more calcium carbonate than will shell waste residual made from shrimp shell, it will take much more acid to demineralize crab shell waste residual than shrimp shell waste residual. In Tables 3.10 and 3.11, it can be seen that the acid demineralization cost for shell waste residual from Maryland/Delaware, an all-crab area, contributes 33–40¢/lb to the cost of chitosan, whereas the shell waste residual from Texas #3, an all-shrimp area, adds an acid demineralization cost of only 13.1–13.7¢ to each pound of chitosan made.

Comment on the results in Tables 3.10 and 3.11 The fourth column of data in Tables 3.10 and 3.11 shows the summation of the three types of costs that vary with the source of shell waste residual. For both tables the various areas producing shell waste residual are listed in order of increasing cost as shown in this column. Given assumption #14 (p. 48), this is the predicted order of preference for the chitosan manufacturer's purchases of shell waste residual from different areas. It should be emphasized that this ordering is highly preliminary; as can be seen from the differences between Tables 3.10 and 3.11, the relative positions of different areas and levels of production on the lists are highly sensitive to the assumptions we have made in estimating various costs. Nevertheless, as new information becomes available this basic technique may be used to reassess the advantage to the chitosan producer of stimulating shell waste residual and protein production in specific areas.

The final two columns of Tables 3.10 and 3.11 show estimates of the quantities of chitosan that can be produced in each area and the cumulative quantities of chitosan that can be produced within the indicated total level of purchase, transport, and acid demineralization costs. The relationship between these columns and the summary cost columns shows how much additional shell waste residual source-related production cost must be incurred to increase chitosan production to different levels. In the following subpart, these increased costs with increasing production will be considered together with potential economies of scale in labor and other costs to form an estimated overall relationship between chitosan production quantity and production cost.

Before proceeding further, however, it will be helpful to clarify the relationship between the figures for the minimum purchase cost for the shell waste residual from each area (the first data columns of Tables 3.10 and 3.11) and probable true sales prices. The minimum purchase costs shown are the lowest shell waste residual prices (under our assumptions) that would justify production in different areas. If the market behaves according to competitive-equilibrium economic models, however, the suppliers of shell waste residual that can support relatively low-cost chitosan production will be able to charge a premium price for their shell waste residual, which will bring the total cost of producing chitosan from their waste up to the cost level for producing chitosan from the highest-cost shell waste residual supplier whose product is required to meet demand. For example, in Table 3.11, the lowest-cost supplier is Virginia operating at one-third potential area production capacity. The Virginia$_{1/3}$ operation can supply shell waste residual to support about 0.21 million pounds of annual chitosan production at a total source-related cost of 84¢/lb, including 40¢/lb of chitosan shell waste residual minimum purchase cost. If, however, the quantity of chitosan to be produced is more than .21 million and up to .39 million pounds, the chitosan producer will need to buy the more expensive Louisiana #1 material and accept total source-related costs of 86¢/lb of chitosan. In this situation, however, the Virginia #1 producer has the option of withholding its shell waste residual from sale unless as much as a 2¢/lb chitosan premium is paid over the 40¢/lb minimum needed to justify production. Under competitive conditions,[999] it will be rational for the chitosan producer to pay up to the 2¢/lb chitosan premium rather than obtain additional material from Louisiana$_{1/3}$ or still higher cost sources.

3.1.5.2 Costs Which Do Not Vary with the Source of Shell Waste Residual, and Overall Costs of Producing Various Quantities of Chitosan Tables 3.12 and 3.13 summarize the remaining costs of chitosan production from shell waste residual at various total levels of chitosan production. As before, Table 3.12 is based on the most optimistic, high quantity/low cost assumptions and Table 3.13 is based on the most pessimistic, low quantity/high cost assumptions. The first two data columns for each table are drawn from the fourth and last data columns of Tables 3.10 and 3.11.

> *Assumption #17: Caustic soda for deacetylation (50% NaOH) must be in amounts that are at least double the volume of the chitin entering the reaction. This implies a weight ratio of approximately five pounds of concentrated caustic per pound of chitosan produced.*

---

[999] i.e. alternative potential chitosan producers who might buy the shell waste residual, or a marginal-value pricing agreement.

TABLE 3.12
Long-Run Average Cost of Producing Various Quantities of Chitosan (Plant hypothetically located in Augusta, Ga.)
High Quantity, Low Cost Assumptions

Planned Annual Chitosan Production Level (Millions of Lbs)	*Costs Which Vary With the Source of Shell Waste Residual*	*¢/lb Chitosan Costs*				
		Caustic Soda for Deacetylation	*Utilities (Highly Conjectural)*	*All Labor*	*10% Depreciation + 20% Return on Investment*	*Total Cost of Chitosan*
0.43	23	35	8	16.6	25.6	108
1.63	25	"	"	9.6	14.7	92
2.71	27	"	"	7.7	11.9	90
3.14	29	"	"	7.3	11.2	90
4.74	34	"	"	6.1	9.4	93
6.23	39	"	"	5.5	8.4	96
8.18	42	"	"	4.9	7.5	97
8.45	55	"	"	4.8	7.4	110
8.53	70	"	"	4.8	7.4	125
8.60	89	"	"	4.8	7.4	144

TABLE 3.13
Long-Run Average Cost of Producing Various Quantities of Chitosan (Plant hypothetically located in Augusta, Ga.)
Low Quantity, High Cost Assumptions

Planned Annual Chitosan Production Level (Millions of Lbs)	*Costs Which Vary With the Source of Shell Waste Residual*	*¢/lb Chitosan Costs*				
		Caustic Soda for Deacetylation	*Utilities (Highly Conjectural)*	*All Labor*	*20% Depreciation + 40% Return on Investment*	*Total Cost of Chitosan*
.39	86	45	11	24	53	219
.71	90	"	"	18.7	42	206
.87	93	"	"	17.2	38	204
1.46	108	"	"	13.8	31	209
1.90	113	"	"	12.4	28	209
2.34	119	"	"	11.4	25	212
2.69	137	"	"	10.7	24	228
3.36	149	"	"	9.8	22	237
4.07	166	"	"	9.0	20	251
4.47	202	"	"	8.7	19.3	286
4.66	259	"	"	8.6	19.0	343
4.75	304	"	"	8.5	18.9	387
4.79	371	"	"	8.5	18.8	454

The cost of caustic soda for deacetylation The quantity of caustic required was estimated on a volume basis rather than a chemical equivalency basis because of the need to maintain a reasonable degree of liquidity for mixing and heating the reaction mixture. At relatively low ratios of caustic soda volume to chitin volume, the mixture is reported to have a consistency similar to bread dough. The amount of caustic soda assumed here is approximately an excess of ten times in purely chemical stoichiometric terms, and it is theoretically possible to recover and reuse some of it. However, we have not attempted to estimate costs for such a recovery procedure and instead assume that all the caustic soda value is lost in the process.

The price of caustic soda is currently about \$140–180/ton[11] (7–9¢/lb). This implies a deacetylation cost of 35–45¢/lb of chitosan produced.

Utilities costs The estimates for this category of costs are very uncertain. They have been based on the general expectation[4] that for a 500,000 lb/year plant the utilities cost would be approximately half the size of the labor cost. Because fuel and electricity requirements for processing operations may be approximately proportional to product output, a flat charge of 8–11¢/lb of chitosan produced has been assumed for utilities costs, regardless of the scale of production.

Costs for labor, depreciation, and minimum required return on investment These costs are also largely speculative. No one has yet built a plant to synthesize chitosan from shell waste residual, and we have not attempted a detailed engineering design to evaluate in detail the capital costs and labor requirements of the various types of process equipment required. Instead, from information on the approximate capital costs and labor requirements of existing installations producing chitosan from wet waste, rough estimates were produced of capital costs and labor requirements for a plant making 500,000 pounds of chitosan per year from shell waste residual. A scaling factor was then selected to extrapolate capital and labor costs to larger and smaller production levels.

> *Assumption #18: A business capable of producing 500,000 lbs of chitosan per year would require six total workers (\$78–108,000 per year total labor cost) and a capital investment of about \$400,000.*

> *Assumption #19: For businesses with capacities larger or smaller than 500,000 lbs chitosan/year, each 50% increase in capital and labor costs yields a doubling of effective capacity and output.*

The scaling factor for Assumption #19 is believed to be relatively conservative — that is, economies of scale (decreases in unit cost) may have been underestimated relative to the norm for general chemical processes.

Assumptions 18 and 19 lead to the following equations for calculating unit labor cost and unit cost for depreciation and minimum return on investment:

$$\text{unit labor cost (¢/lb chitosan)} = \frac{7.8 \times 10^6 - 1.08 \times 10^7\text{¢}}{(\#\text{lbs capacity})^{.415}(5 \times 10^5\ \text{lbs})^{.585}}$$

unit cost of depreciation + minimum
required return on investment (¢/lb chitosan) =

$$\frac{1.2 \times 10^7 - 2.4 \times 10^7\text{¢}}{(\#\ \text{lbs capacity})^{.415}(5 \times 10^5\text{lbs})^{.585}}$$

Comment on the results in Tables 3.11 and 3.12 The combination of the first and last columns of Tables 3.11 and 3.12 constitutes an estimated range for the long run supply function for chitosan production from shellfish waste in the U.S. Optimistic and pessimistic estimates of the supply function are shown as the lower and upper lines of Figure 3.3 (p. 56). From this we can con-

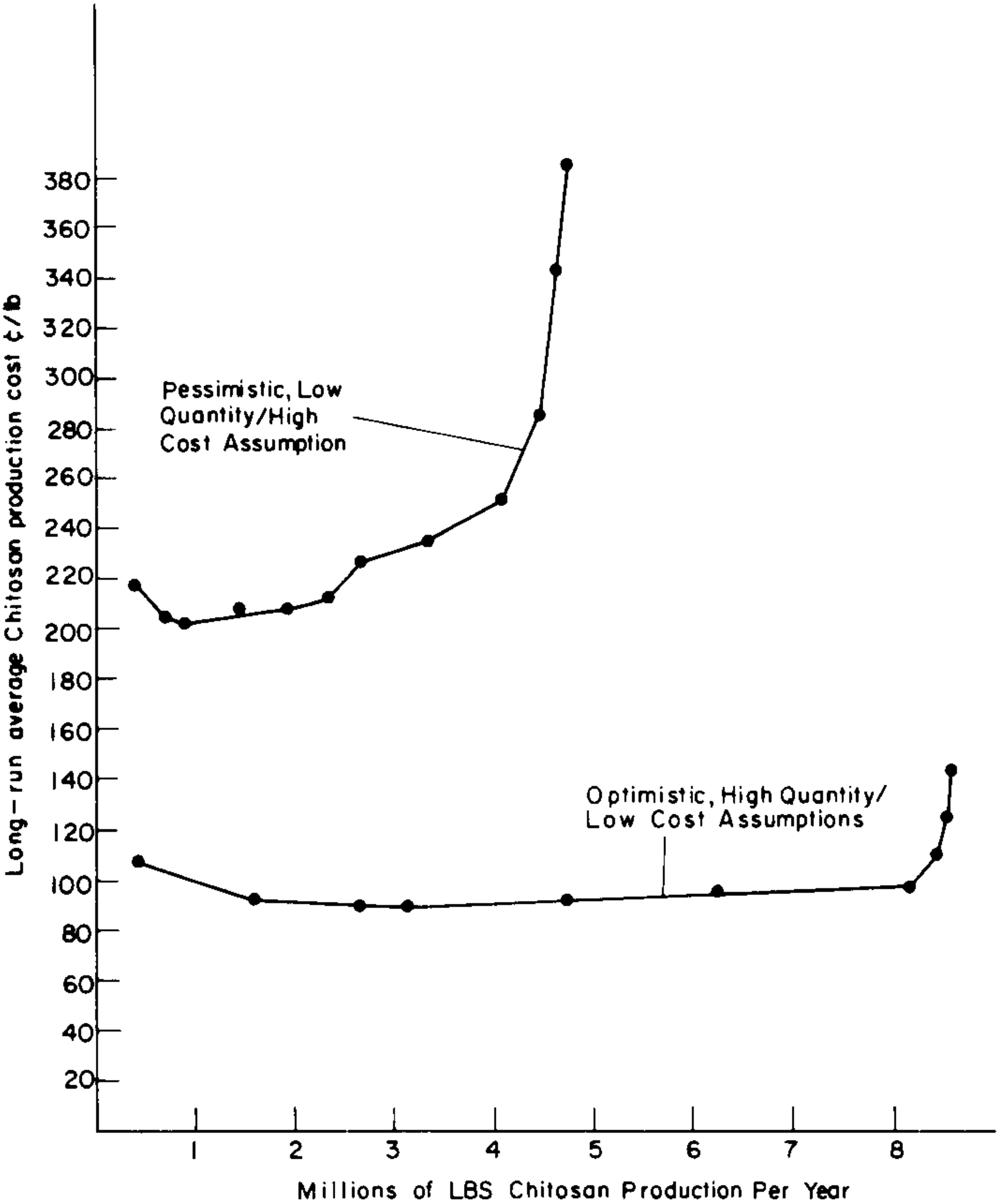
Long-run average Chitosan production cost ¢/lb
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
Pessimistic, Low Quantity/High Cost Assumption
Optimistic, High Quantity/ Low Cost Assumptions
1
2
3
4
5
6
7
8
Millions of LBS Chitosan Production Per Year

FIGURE 3.3

clude that chitosan production of between one and four million pounds per year is likely to be feasible with 20–40% return on capital investment at chitosan selling prices somewhere between $1.00–2.50 per pound. Section 4 presents an assessment of the likelihood that the market would absorb those quantities of chitosan if offered in that price range.

3.2 Potential for Production of Chitin from Fungal Waste

If strong markets for chitin or chitosan were to develop that could not be adequately supplied by the limited quantities of chitin available from shrimp and crab waste, the next most likely source of chitin would be fungi. Many fungi are reported to contain chitin as a substantial constituent of the dry weight of their cell walls[hhh]. In fungi, however, the chitin is associated with various other types of polysaccharides that may prove difficult or expensive to remove completely. Because there has been no exploration of model industrial extraction systems, it is not possible to ascertain potential production costs at this time.

Nevertheless, the large quantities of fungi currently grown in fermentation systems (producing organic acids, antibiotics, and enzymes) constitute a potential source of chitin that should not be entirely neglected. The largest single chemical made in fermentation systems is citric acid. It has been estimated[12] that the 1973 production of citric acid was 180 million pounds. The fermentation that produces citric acid is known to be very highly efficient (50–70% of the sugar fed to the fungi appears as citric acid[17]) so it is unlikely that the fungal waste by-product from national citric acid production is as much as 100 million pounds, but it is possible that a few tens of millions of pounds of fungal waste are produced in citric acid plants annually. Moreover, since the organism used for citric acid manufacture is *Aspergillus niger*, which has a substantial chitin content,[13] citric acid plants may do well eventually to explore the potential for chitin production if shellfish chitin proves marketable.

3.3 Other Potential Sources of Chitin

An interesting possibility for long-term exploration is the potential of certain marine diatoms that apparently secrete filaments of nearly pure chitin that can easily be harvested from a growth medium.[7] Development of this potential, however, must await additional research on the growth characteristics of organisms of this type and on minimal cost nutritional requirements, quantitative yield of chitin, and precautions against viral and bacterial parisitism or contamination of industrial cultures.

Finally, some production of chitin may be feasible from insect sources. Insects are currently raised for programs of biological control of certain insect pests, such as the screwworm fly in some southern and western states, and at least one pest of cotton in California and Arizona. The screwworm fly program yields a by-product of pupal cases as the flies complete their metamorphosis from maggots to adults. These cases might be treated in a similar fashion to shellfish waste. We have no data on the quantity available, but the tonnage is probably small. Insect-based production has also been suggested (with less than complete seriousness) through institution of cockroach farming, but it can be anticipated that production based on microorganisms will pose fewer economic and technical difficulties than comparable operations based on cockroaches.

[hhh] Stagg and Feather[13] find that the dry cell wall of *Aspergillus niger* is 42% chitin. Work with other *Aspergillus* species and different conditions[14, 15] indicates chitin/dry cell wall contents of 14–18%. *Mucor rouxii* is of particular interest because its cell wall contains more chitosan than chitin and the ratio of chitosan + chitin/dry cell wall is apparently in the range of 36–42%. From the latter paper, it is also of interest to note that the cell wall constitutes 14–18% of the dry weight of the whole cell — leading to the inference that chitosan + chitin is approximately 6–7% of the dry weight of the whole cell in this species. Additional data for chitin content of fungi and other organisms can be found in a thesis by Kong[7].

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4 ANALYSIS OF POSSIBLE DEMAND

The task of this section is to determine at what price chitin and chitin derivatives are likely to sell, if various quantities are offered to the market. In economists' terminology, we wish to estimate the long-run demand function.

As noted in Chapter 3, the techniques most often used by economists for inferring supply or demand functions depend on observing the history of past market action. Since this type of information is essentially nonexistent for the case of chitin and chitosan, this section will use two different approaches to derive some expectations of likely future demand:

> 1) The first part of this section will be an historical examination of overall relationships between price and quantity for selected groups of commercial polymers. By observing the precedents set by other materials, we may infer an approximate market potential for chitin/chitosan as a function of price, if these products find a spectrum of uses similar in function and value to those of known successful polymers.
>
> 2) The second part of this section will examine the probable market potential for some individual types of applications.

4.1 Relationships Between Price and Quantity for Selected Groups of Commercial Polymers

Figures 4.1 to 4.4 show examples of price-quantity relationships for four quite different polymer groups: general plastics, specialty plastics, cellulosics, and water-soluble gums and starches. Each figure shows the *cumulative quantity* of all the different polymers in that polymer group that sold at or above a given price.[a] This kind of plot gives us some idea of the *distribution of uses*[b] for these materials that have supported given price-premiums over the cheapest substances in the category. If a chitin derivative is technically successful in performing some of the functions now carried out by these materials, we can expect that it may, with effort, capture some quantity of the market to the left of each line at some price below the line.

For three of the polymer groups, the general price-quantity relationship appears to be roughly log-linear (linear change in price for logarithmic change in quantity sold) whereas for the gums and starches the relationship appears to be more nearly log-log. We do not have a theoretical framework to explain either type of behavior.

However, in examining data-plots for the same *polymer groups* as in Figures 4.1–4.4 for various years, we find that when adjusted for inflation with the U.S. wholesale price index, these overall relationships appear to be relatively constant over time. For example, Table 4.1 shows the prices (corrected to April 1976 dollars) corresponding to one and ten million pound per year quantities of the various polymer groups inferred from the price-quantity plots for different years. It can be seen that, for constant quantity, the price predicted from the data for different years is essentially the same.

The appropriateness of any polymer group for predicting probable price-quantity relationships of chitin derivatives must depend on a judgment of whether chitin derivatives are likely to find application at least as economically valuable as current, successful members of the predic-

---

[a] For example, in the "Gums and Starches" plot, Figure 4.4, the total quantity of polymer selling at or above $2.40 per pound is the sum of the quantities of tragacanth, agar, and pectin sold, or about 12 million pounds.

[b] It is *not*, strictly speaking, an economic demand curve.

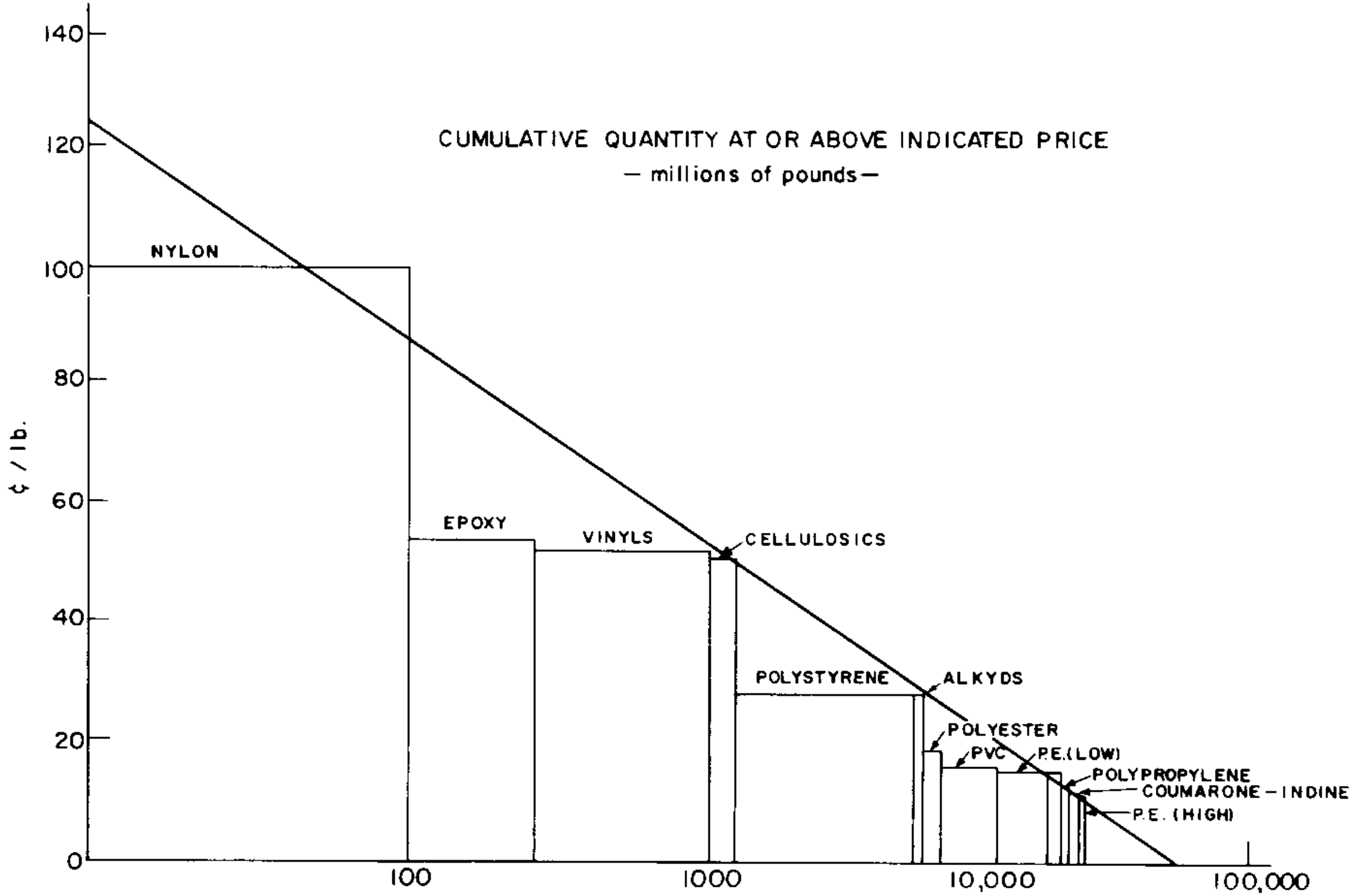

FIGURE 4.1 General Plastics 1972

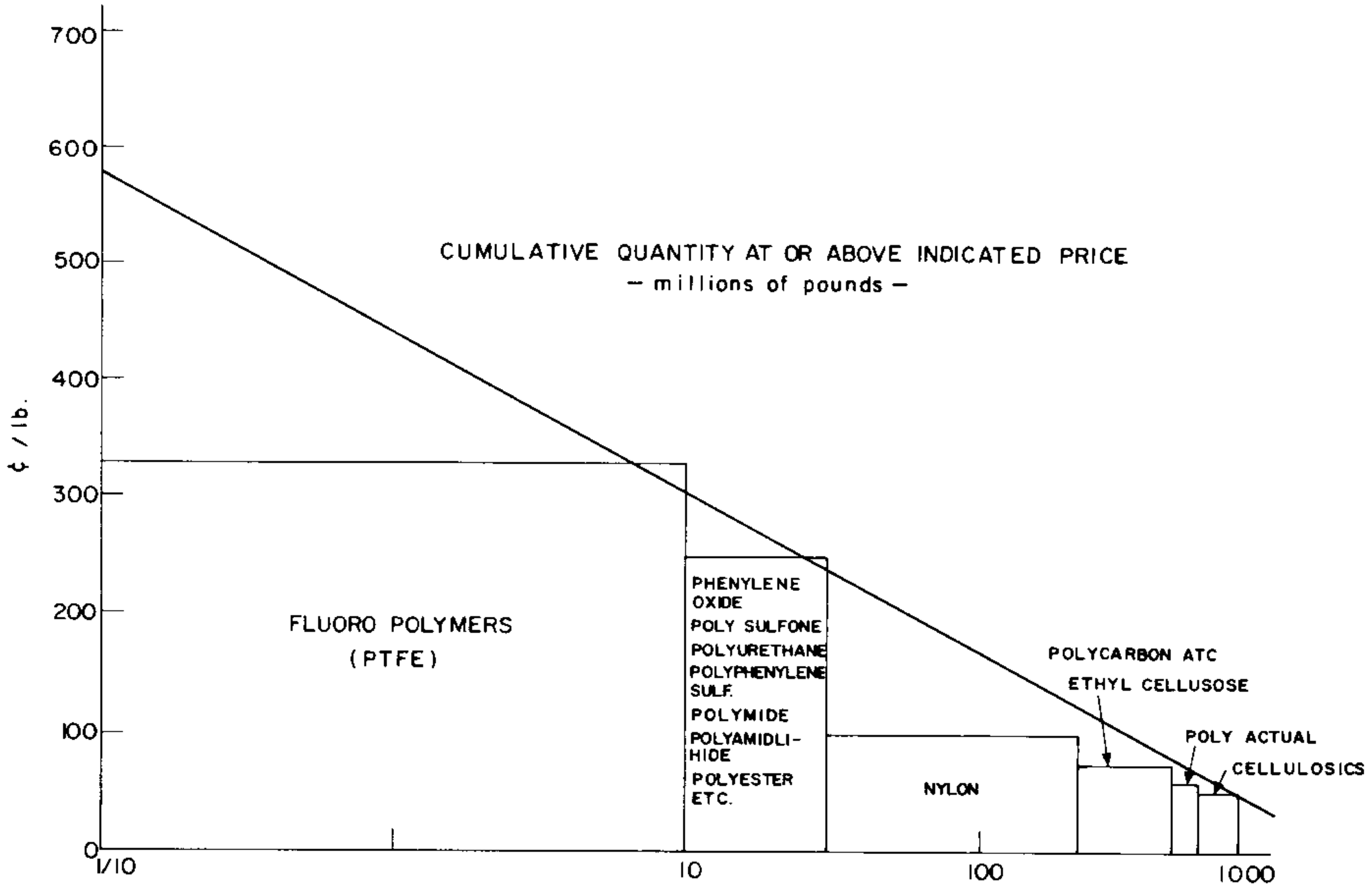

FIGURE 4.2 Specialty Polymers 1973

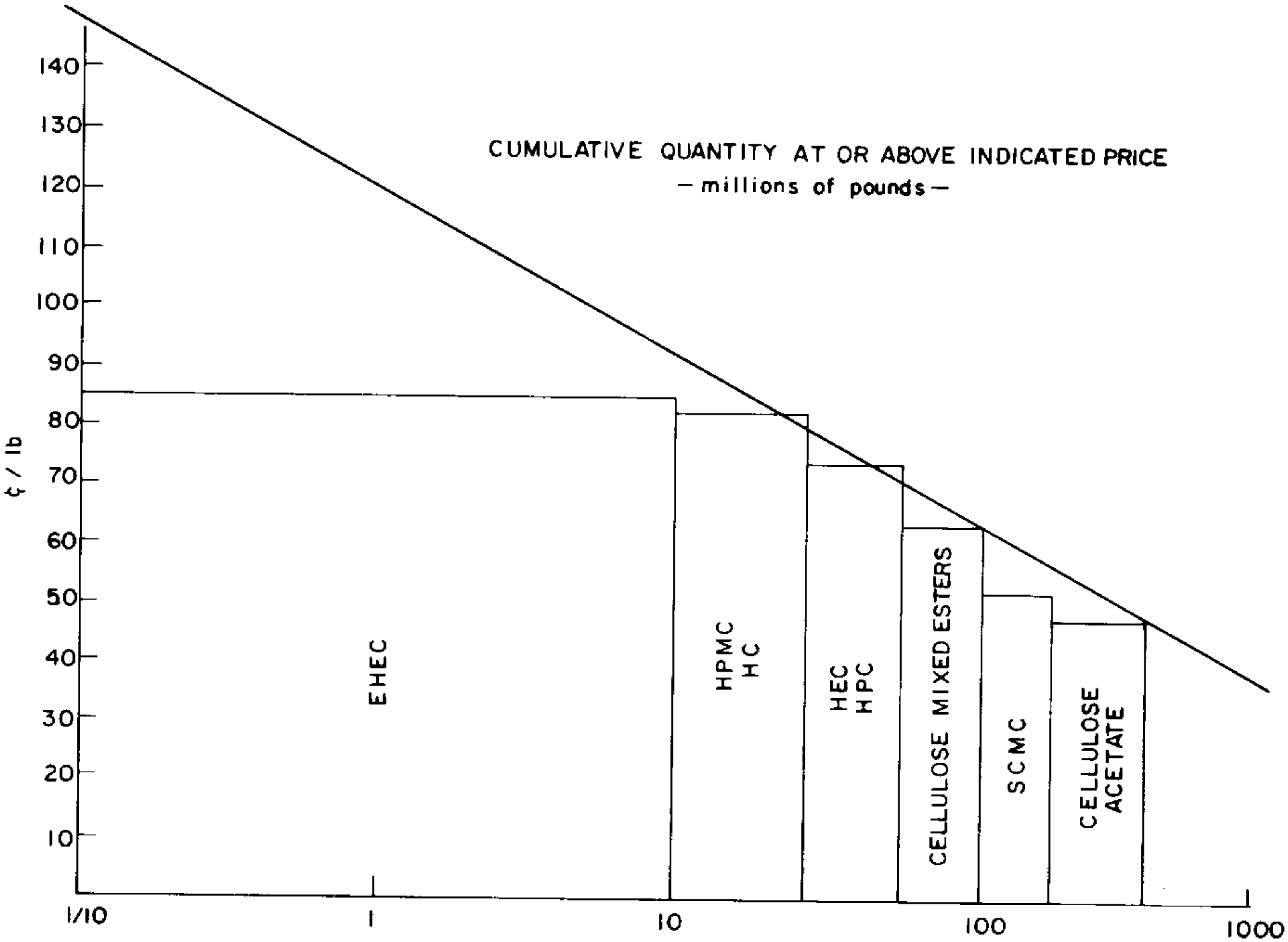

FIGURE 4.3 Cellulosics 1973

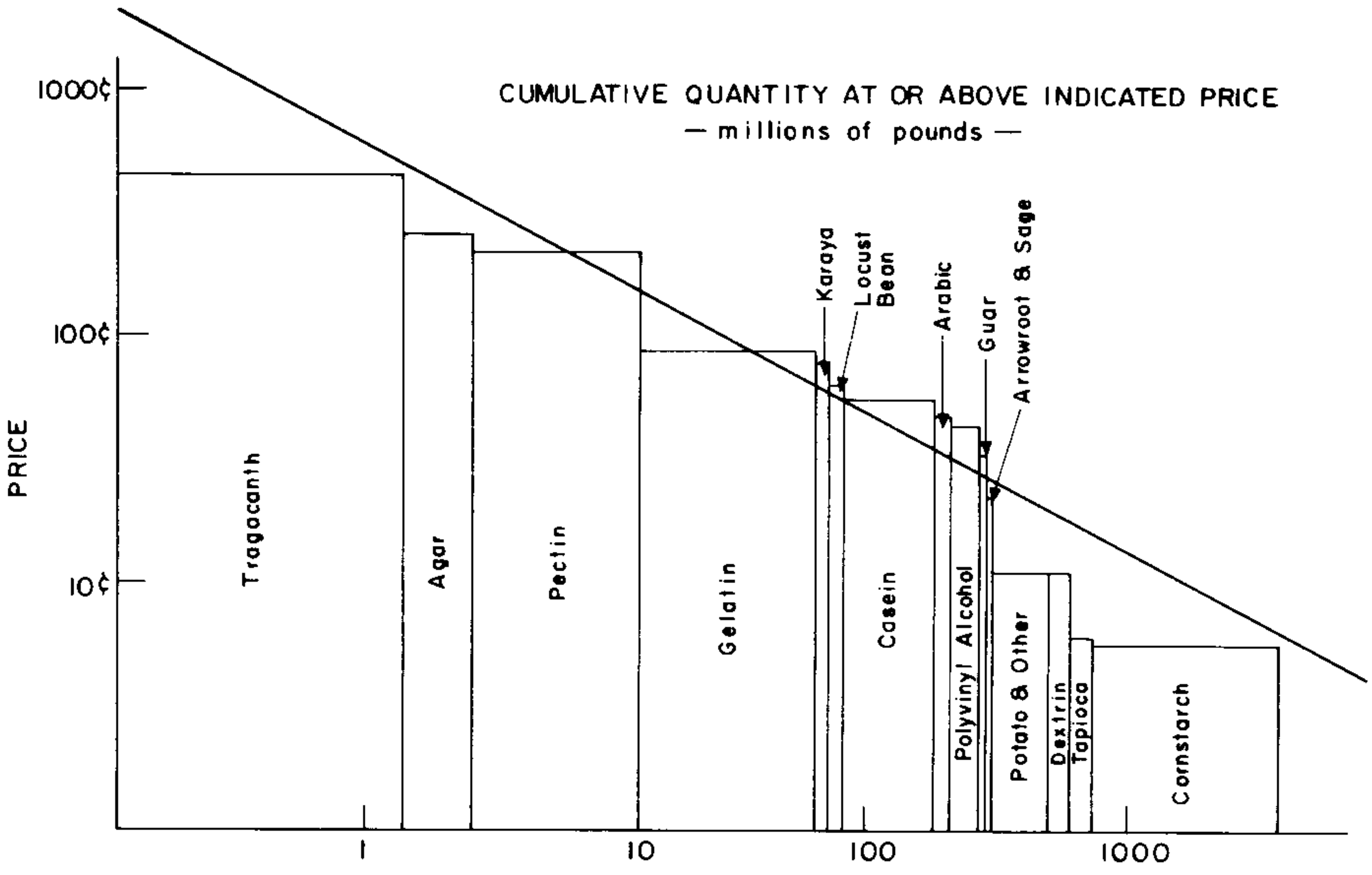

FIGURE 4.4 Water-Soluble Resins, Gums and Starches 1972

TABLE 4.1
Price-Quantity Relationships for Different Polymer Groups—Derived from Sales Data for Various Years

		*Indicated Selling Price of the Most Expensive (April 1976 dollars)**	
Polymer Group	*Year of Data*	*1 million pound quantity in group*	*10 million pound quantity in group*
General Plastics	1972	2.40	1.90
	1970	2.30	1.80
	1965	2.70	2.00
	1960	2.50	1.90
	1955	2.30	1.80
Specialty Plastics	1973	5.90	4.10
	1972	7.20	5.00
	1971	6.40	4.40
Cellulosics	1974	1.90	1.50
	1973	1.60	1.20
	1972	1.70	1.30
	1969	1.90	1.50
	1965	1.90	1.50
	1955	1.80	1.40
Gums & Starches	1972	9.10	2.60
	1967	7.40**	2.40**
	1963	6.70**	2.50**

*Adjusted with U.S. wholesale price index for all commodities.

**Very approximate values -- price-quantity relationships not well described as linear, even on log-log plots.

tor group. The two groups that, on structural grounds, are most similar to chitin derivatives are cellulosics and gums and starches. It is worthy of note that for the modest chitin production levels likely to be attainable in the U.S., the two groups suggest quite different potential prices. However, an important caveat must be attached to the use of the gums and starches polymer group as a potential precedent for future chitosan markets. Many of the most expensive members of the gums and starches group find primary usage in food as thickeners, stabilizers, etc. Chitin derivatives cannot be expected to find uses in food for some time because the long-term toxicological studies required for approval as a food additive have not yet been initiated.

However, even at the conservative price levels suggested by comparison with the cellulosic polymer group, there appears to be a reasonable expectation that the market can absorb several million pounds of cellulosic polymer at prices between $1.60–$1.90 per pound. This range is somewhat below the price needed to induce chitosan production under the most pessimistic set of assumptions on production costs, but it is above the midpoint of the range between the optimistic and pessimistic production assumptions. There is thus an indication that chitin production can be economically viable, even if it commands prices no higher than would be expected for the general cellulosics comparison group.

4.2 Potential Demand for Selected Applications

The previous part was a very general projection of probable market behavior based on the past record of polymers with similarity to chitin derivatives. The ultimate question, however, which cannot be resolved with the information currently available, is whether or not the specific properties of a chitin derivative will enable it to perform specific economically valuable functions at prices competitive with alternative materials for those functions. Table 4.2 lists

TABLE 4.2
Suggested Applications for Chitosan

Property	*Uses*
High charge density and potential binding capacity (relative to other substituted celluloses)	Ion-exchange or chelating solids for chromatography, metal recovery from waste streams, industrial process water purification for recycling, etc.
Film-forming	Ion-exchange membranes for electrodialysis
Coagulation	Waste water treatment
Strong binding to negatively-charged polymeric products	Paper-strength additive, dye binder for textiles, binding agent for nonwoven fabrics, sausage-casing component, adhesives
Wound-healing promotion, nonthrombogenic	Wound treatments, surgical adjuncts

five important properties of chitosan and the major types of economic uses that depend on those properties. Below, we shall summarize some characteristics of the market potential implied by each set of uses. In nearly all cases, good comparative cost-effectiveness data indicating the relative technical performance of chitosan and its major competitors for each function are lacking. Because of this, the summary is incomplete and necessarily speculative.

4.2.1 Ion-Exchange and Chelating Applications

Ion-exchange materials have a very broad spectrum of current applications in the purification of water entering industrial processes, in wastewater purification, and in separation of dissolved materials by chromatography. Broadly, there are four types of ion-exchange substances as defined by their molecular charge characteristics.

- strong acid — usually sulfonic acid derivatives, negatively charged even at low pH
- weak acid — usually carboxylic acid derivatives, which lose their negative charge at low pH
- strong base — usually quaternary amine derivatives, which retain a positive charge even at high pH
- weak base — primary, secondary, or tertiary amine derivatives, which lose their positive charge and become chelating substances at high pH. Chitosan is in this category.

Currently, many ion-exchange compounds of all four types are synthesized from styrene-divinyl benzene. Information from one source[1] indicates that on the order of twenty million pounds of styrene-divinyl benzene ion-exchange resins were exported from the U.S. in recent years, and it seems likely that the domestic market may be several times this quantity.

Table 4.3 lists the properties and (1974) prices of several weak base ion-exchange resins currently marketed by Rohm & Haas. Assuming a binding capacity of about 5 milliequivalents per dry gram for chitosan (equivalent to about 80% deacetylation), Table 4.3 also shows the results of a computation of the ion-exchange value of chitosan on an equal binding capacity basis. This calculation assumes that chitosan products can be made with flow, durability, and other desirable properties comparable to the Amberlites. If these assumptions are correct, the range of presumptive selling prices on this market ($2.35–6.41) is quite encouraging, considering that the market could absorb several million pounds.

TABLE 4.3
Properties and 1974 Prices of Rohm & Haas Ion Exchange Resins*

	Weakly Basic Anion Exchange Resins							*Binding Capacity*	
			Price (Truckload-900 ft^3)						
Resin Name	*Macro-Reticular or Gel-Type*	*Shipping Weight (lb/cu.ft.)*	*\$/cu.ft. (12/9/74)*	*\$/wet lb*	*Moisture Content (%)*	*Apparent Wet Density gm/cc*	*Dry Weight (g) Per Wet cc*	*meg/cc Wet*	*meg/dry g (Approx.)*
Amberlite IR–45	GEL	42	106.00	2.52	40–45	.67	.3685–.402	1.90	4.73– 5.16
Amberlite IRA–47	GEL	45	70.35	1.56	64–68	.67	.2144–.2412	1.7	7.05– 7.93
Amberlite IRA–47S	GEL	42	70.35	1.675	66–70	.67	.201–.2278	2.4	10.54–11.94
Amberlite IRA–68	GEL	45	104.00	2.31	57–63	.72	.2664–.3096	1.60	5.17– 6.01
Amberlite IRA–49	GEL	41	95.00	2.32	66–70	.65	.195 –.221	2.5	11.31–12.82
Amberlite IR–48	GEL	35	94.00	2.69	42–47	.58	.3074–.3364	3.2	9.51–10.41
Amberlite IRA–93	MR	38	94.00	2.47	46–54	.61	.2806–.3294	1.25	3.79– 4.45
Amberlite IRA–96	MR	40	96.00	2.4	54–58	.61	.2562–.2806	1.2	4.28– 4.68

*Sources: Rohm and Haas Company, "Amberlite^R Ion Exchange Resins and Other Fluid Process Chemicals — Summary Chart of Properties and Applications," *Amber-Hi-Lites*, No. 141, (July 1974).

Price	*Price/Binding Capacity*		*Equivalent Price ($1/lb) Chitosan*		
$/dry lb	*¢/ml*	*¢/meg*	*At Equivalent Binding Capacity (Assuming Chitosan at ~ 5 meg/dry gram)*	*Remarks*	*Applications*
4.21–4.59	.3743	.1970	4.47	Used in conjunction with a cation exchange resin in the hydrogen form, will effectively remove anions of strong acids. Ammonia is the recommended regenerant.	Deacidification, deionization of water where only the removal of strong acids is desired, and deionization of process liquors in chemical, pharmaceutical and food industries.
4.34–4.89	.2484	.1461	3.32	A condensate weak-base type resin for use in those applications not requiring the unsurpassed oxidative stability and resistance to organic fouling of the weakly basic, macroeticular anion exchange resin, Amberlite IRA–93. Since this resin contains a significant number of strongly basic groups, it is often referred to as an intermediate base resin.	Deionization systems as well as in a variety of other applications including pharmaceutical, sugar, and chemical processing since it offers a high acid neutralizing capacity at low cost.
4.93–9.58	.2484	.1035	2.35	A more porous version of Amberlite IRA–47.	Deionization and decolorization of beet and pineapple sugar liquors.
5.37–6.25	.3673	.2295	5.21	Has an unusually high capacity for large organic molecules. Also, it can be operated in the bicarbonate form to exchange bicarbonate for anions of strong mineral acids.	Deacidification, deionization, and desalination of water where the removal of strong mineral acids and adsorption of organics is desired, deionization of process liquors; isolation of acidic natural products.
6.81–7.72	.3355	.1342	3.05	Primarily a tertiary amine epoxy-based exchanger.	Deionization of high TDS water supplies.
4.63–5.07	.3320	.1037	2.35	A phenolic-based polyamine condensate having a very high exchange capacity.	Used primarily in the pharmaceutical industry for the recovery and purification of amino acids.
4.58–5.38	.3320	.2656	6.03	Has excellent resistance to oxidation. Also, has high exchange capacity and exceptional resistance to organic fouling. Often used because of the long operating life that can be expected.	Deacidification, deionization of water (where the removal of strong mineral organic acids is desired), deionization of process liquors. Performance of this resin is outstanding in the removal of organic material from surface water supplies. Sugar deashing & decolorization.
5.22–5.71	.3390	.2825	6.41	Has all of the major attributes of Amberlite IRA–93 plus improved kinetics & physical stability.	Deionization of surface waters & high TDS effluent. Uniquely suitable for use in Amberlite MB–4 resin system.

Rohm and Haas Company, "Price Schedule", (AMBERLITE and AMBERLYST Ion Exchange Resins — End-User Prices for Applications other than Water Conditioning, EFFECTIVE DATE: December 9, 1974.

While it does not appear that chitin or chitosan have yet been commercially adopted in ion-exchange applications, a number of preliminary technical evaluations have been performed indicating good, and often superior, capability in such functions. Chitosan is noteworthy for its affinity for certain metal ions that are generally located near the center of the periodic table, and this affinity is virtually unaffected by the presence of alkali metal ions such as sodium or potassium. Consequently, it is remarkably effective for the collection or for quantitative determination of metals such as mercury or vanadium in sea water or industrial brine,[1] or for the collection or preconcentration of zinc, copper, cadmium, or lead from sea water.[2]

The differential affinity of chitosan for transition metals, as opposed to alkali metals, can assist in the determination of radioactive cesium, an important indicator in nuclear fuel solutions, by allowing for the easy removal of zirconium and other radioactive elements that interfere with the measurement.[3] High resistance to radiation injury contributes to chitosan's capability for this suggested use, as well as for a number of other applications in the atomic energy field, including the decontamination of atomic waste waters.

Various other uses are suggested by available data on chitosan's metal binding capacity, but such suggestions need further elaboration and would benefit from specific evaluation under actual industrial conditions and in comparison with realistic alternatives. One modest suggestion is related to chromium recovery from plating bath rinse water from small plating operations. Chitosan can chelate trivalent or hexavalent chromium and, at pH less than 2.5 or greater than 5.5, can separate these two forms. The theoretical capacity of one equivalent of chromium per equivalent of glucosamine in the polymer molecule represents 26 grams of chromium for every 100 grams of chitosan, a capacity which appears to be double the maximum capacity obtained in recent experiments with activated carbon beds.[4] Both types of column or cartridge bed can be regenerated by elution techniques, would permit simple continuous operation in minimum floor space, and would require low original investment. Further comparisons are needed to determine which is the better choice.

A considerable number of technical capabilities are known for chitosan or chitin in the chelating, ion-exchange, chromatography field, but most of these need to be more specifically studied with respect to specific commercial applications. Among these applications are the collection or removal of anions like cyanide or phosphate on columns or cartridges of suitable chitosan-metal chelates, the commercial purification of biologicals, such as thyroglobulin, wheat germ agglutinin, or nucleic acid constituents, or general laboratory utility in biochemical research.

4.2.2 *Coagulation Applications*

Chitosan is presently employed in small domestic sewage treatment systems,[c] in conjunction with other settling aids such as alum or bentonite clay, to promote coagulation and settling of colloidal and other fine suspended solids. In this procedure, the polyelectrolyte is added at the rate of 1–2 ppm, but could be employed alone, without alum, if the concentration were raised to around 10 ppm.

Similar applications in the removal of solids from food processing wastewater, or in the conditioning of activated brewery or vegetable sludge, have been tested[5] and have yielded favorable comparisons with competing polymers selling in the range of $1.50 to $3.00 per pound. This price range brackets a 1976 price range ($2.12 to $2.72 per pound) of chitosan in Japan, where about 50 metric tons per month are consumed, almost entirely as a flocculation aid for the treatment of food processing wastes.[6]

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[c] Environmental Systems, Inc., Seattle.

4.2.3 *Film and Fiber Applications*

Despite the considerable long-term interest in chitin-derived films, their technical characteristics are still poorly defined and must await better quality control before applications can be precisely defined and market estimates can become very meaningful. Chitin-derived fibers are also in this category, sharing with film certain aspects of production techniques, related mechanical properties, and a sparse, nonuniform body of knowledge on what exactly those properties are or might be. However, what is either known or tentatively established suggests some interesting possibilities.

Since chitin will probably be a moderately high-priced, low-volume commodity, it apparently must seek low-volume, high-valued applications in which the value it adds to the product can easily offset the cost. Applications of this nature that have interested investigators include sutures and other surgical adjuncts, special food casings or wraps, and ion exchange membranes.

4.2.3.1. Meat Casings A continuing percentage of new patents in food technology are developments of new sausage casings striving for a share of a substantial worldwide market. Some of these are quite expensive, but are able to compete with types that, though generally cheaper, have lower appeal for various reasons, including the degree to which they permit cost savings by automating the making of sausage. Thus, casings that can be *shirred*, or crumpled to between 1/35 and 1/100 of their flat, stretched length, can be crammed onto the feed horn of an automatic stuffing machine. Breathable casings allow the escape of drippings and the entry of smoke during meat curing. Others, such as reconstituted collagen, bind tightly to the meat and shrink with it during cooking or smoking. Collagen types are nominally edible although heavier forms are too tough for chewing. Other characteristics distinguish the remaining varieties.

The cheapest types of man-made casings are polyester and those varieties of cellulose used in ordinary hot dog manufacture. They run between $\$0.12 \times 10^{-3}$ and $\$0.22 \times 10^{-3}$ per square inch and, for polyester, between \$2.80 and \$5.30 per pound of casing. Fibrous casings cost from $\$0.42 \times 10^{-3}$ to $\$0.82 \times 10^{-3}$ per square inch, while collagen products top the scale at about $\$11.0 \times 10^{-3}$ per square inch. Clearly, technical or other types of advantages are capable of supporting quite large price differentials in these materials and allow for the possible entry of other moderately expensive films of suitable characteristics.

Since natural chitin is edible,[d] it should be expected that the edibility of reconstituted forms would be limited only by plasticizers, residual solvents, or other such additives or contaminants. Testing of other characteristics of reconstituted chitin that might be useful in this field is dependent upon further development of solvent and casting systems[e] from which pure or plasticized chitin films can be made. However, a number of chitin *derivatives* can be solubilized and will produce films. Except for chitosan-alginate films, which have already brought one patent in meat casings,[f,10] this field is not well explored.

Market information on casings is regarded as too competitively valuable for release by firms in this business, but simple indirect reasoning may be applied to obtain a crude assessment of the meat casing market. Since U.S. beef and pork production is on the order of one quarter of the world total,[11] one might anticipate that, as a crude approximation, one quarter of the world sausage casing market may be located here. About 20% of this casing market is served by natural (gut) materials, and the rest by manufactured varieties. A large portion of their market is accounted for by the enormous production of frankfurters, which is on the order of a

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[d] Considerable amounts are consumed in sautéed soft shell crabs.

[e] For instance see references 5, 6, 7.

[f] U.S. Pat. 2,973,274 (1961), reference 10. As described in Karmas, E. *Sausage Casing Technology*, Noyes Data Corp., Park Ridge, N.J. (1974), these casings are edible but exhibit radically improved stability in the presence of sodium salts.

billion pounds per year. The remainder of the market belongs to an assortment of fibrous, polyester, and reconstituted collagen materials. Although all three are quite different in some respects, their capabilities overlap somewhat, so that a compound such as chitin or one of its derivatives, if made in both permeable and impermeable films, might able to substitute for a fraction of all of them. From a surface area requirement, an upper limit for the potential demand can be estimated on the assumption that the quantity of casing material used in frankfurter manufacture probably exceeds any demand that could be generated by a new type of casing. This quantity can be readily estimated:

$$10^9 \text{ lbs} \times 12 \text{ franks per lb} \times 12.6 \text{ in}^2 \text{ per frank} = 151.2 \times 10^9 \text{ in}^2 \text{ surface area.}$$

Assuming 0.4×10^{-4} lbs per in^2, this amounts to $151.2 \times 10^9 \times 0.4 \times 10^{-4} = 6 \times 10^6$ pounds.

4.2.3.2. Absorbable Sutures and Other Surgical Adjuncts Among the specialty products derived from natural and synthetic fibers are surgical sutures. These bear an especially interesting relationship to speculations on the possible use of chitin because of its fiber forming capacity, its natural origin, and its capability of being absorbed by the body. Chitin is known to promote healing of surgical wounds, and its physical properties are amenable to manipulation by chemical derivatization. Thus, some of the technology related to sausage casing development is applicable to the development of sutures.

Absorbable sutures possess about half of the suture market and have a current U.S. value of more than $63 million per year. They are supporting very high prices[9] if calculated on a weight basis, reflecting little sensitivity to the cost of materials. If chitin or a derivative can provide the appropriate technical advantages, this market would represent an ideal match for chitin's modest supply potential and moderately high price.

Any new absorbable suture material would presently be competing with three basic categories: natural gut, reconstituted collagen, and synthetics such as polyglycolic acid, all of which have some disadvantage that makes them vulnerable to competition. The ideal suture would be a monofilament (not requiring braids or twisted strands that could harbor bacteria), would have no undesirable active effect on the patient, and would disappear completely and spontaneously when its job was done. Monofilaments should not only have adequate strength and flexibility, but also good visibility in tissue and nonslip knot security. All present suture materials, and especially gut filaments (96–98% collagen) sometimes cause a tissue reaction. Reconstituted collagen, which is purer than natural gut, is good in fine sizes but is too stiff for larger diameters. Synthetics that are absorbable do not have the flexibility needed for monofilament use, and must be braided. For pure chitin, absorbability and physiological passivity are relatively well assured. What is required is the development and demonstration of satisfactory mechanical properties in monofilament forms. Chemical derivations, on the other hand, must be shown to be absorbable. Generally speaking, derivatives such as ethyl chitin, hydroxyethyl chitin, or carboxymethyl chitin are substrates for lysozyme, while deacetylated, or chitosan, derivates are not. Thus, it could be anticipated that the acetylated forms of chitin or its derivatives would be readily absorbable, but otherwise highly interesting derivatives like the chitosan-alginate materials mentioned for sausage casings might prove not to be.

4.2.4 *Paper and Pulp-Making Applications*

Several materials cheaper than chitosan are available as pulp additives to increase interfiber bonding or to serve as retention aids for fillers and pigments. However, because of its theoretical superiority, chitosan may demonstrate an actual superiority in certain specific paper grades or formulations. On this reasonable probability it has been suggested[12] that a price of

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[9] "Catgut" or synthetic absorbable sutures cost from $0.45 to $0.70 for single 18–54 inch lengths. Microsutures, with needle attached, can range up to $7 for a 5-inch length.

$2.00 per pound could make chitosan both technically and economically desirable in selected applications.

Specialty papers, including tissues of all kinds, easily make up 10% of the total paper maket in this country.[13] Many of these papers have physical requirements for which a chitin derivative additive would be technically useful. One example is electrical insulating papers, for which there is a continuing need for innovation and which have drawn some foreign interest to chitin.[14] Other specialty types of papers span a very large spectrum to include *glassines*, coated and laminated varieties, xerographic grades, cigarette papers, carbon and carbonless copy grades, water-resistant offset printing grades, and others for which chitosan's characteristics are at least suggestive. Altogether, these amount to about 4.1 million tons.[h] Hence, even a fraction of this market as small as 1% would be a worthwhile goal, since it could absorb 820,000 pounds of chitin derivative added at the 1% level.[i]

The current size of the U.S. paper and paperboard market[j] is approximately 65 million tons, with paper alone representing about half of that. By 1980, total consumption is projected to be 82 million tons, implying a paper demand of 41 million tons if the paper-to-board ratio remains fixed. The present content of recycled waste paper is 18–20% and by 1980 will be higher. Inasmuch as recycled fiber does not bind well, and generally needs assistance from additives or fresh binder fibers, this fraction, representing about 9 million tons, may be of special interest in computing additive market potentials.

A recent innovation, the thermomechanical (TM) pulp process may also be of special interest in this regard. Through this process, it is possible to obtain in much greater yield a very good paper-making fiber capable of replacing some of the expensive chemical pulps needed for high strength sheets and for addition to cheaper pulps. Some of the applications for TM pulp could benefit (technically) from the additional binding or filler-retaining properties of chitosan, and most of these are in specialty paper categories. However, the potential of the newsprint market deserves at least some consideration.

Some in the industry hope that perhaps 50% of the chemical (sulfite) pulp, now added at the rate of 20% to increase sheet strength, may be replaced by TM pulp. If the cost-saving potential of the TM process provides a margin in which the cost of chitosan can be absorbed, the addition of chitosan to upgrade some of this newsprint still further might become economically feasible. At a price of $340 per ton, the cost of chemical pulp added at the 20% rate is on the order of $68 per ton of newsprint, while the cost of 10% TM pulp plus 10% chemical pulp would be on the order of ($10 + $34 =) $44, a saving of $24. At a price of $2.00 per pound, chitosan added at a 1% rate would cost $40 per ton of paper. Thus, whether some combination of chitosan with TM pulp could prove economically and technically advantageous would depend upon an additional quantity of chemical pulp that might be displaced and upon any improvement in production rate or other cost-determining resultants.

At least two other possible methods for using chitosan may be considered. One is its application directly to the surface of paper, by means of a size press or surface spray, that might improve the paper's surface strength for applications like offset printing, and that might require substantially less than a 1% addition to the total paper weight. Another is the use of chitosan as a polyelectrolyte in the Saveall apparatus, or other portions of the waste water stream, to improve recovery of valuable fine binder fibers for addition back into the pulp mix. While the amount of chitosan itself added back with the fiber might be too small to affect substantially the paper strength, its presence on the fibers would at the very least be highly compatible.

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[h] 1980 projection.

[i] Chitosan, as a pulp additive for improvement of burst strength of groundwood papers, would be used at about the 1% level.

[j] Apparent consumption. *Statistical Abstract of the U.S., 1975*, U.S. Dept. of Commerce, Bureau of the Census.

4.2.5 *Wound Healing Accelerators and Temporary Prostheses*

For some years, Dr. J. F. Prudden, a physician at Presbyterian Hospital, Dr. Leslie Balassa, a chemist, and investigators associated with them have been studying the wound-healing effects of cartilage or chitin preparations. Some years ago it was discovered that cartilage powders applied to surgical incisions substantially accelerated the healing and strengthened the joining of the edges of these wounds during the early healing process.[k] Subsequently, it was found that the ingredient, N-acetylglucosamine, was essential to this action of cartilage, and wound-healing discoveries and studies were extended to chitin, a slowly degradable polymer of N-acetylglucosamine. As a result of these studies approximately 15 U.S. patents[l] were obtained in the years 1968–1976, of which five relate to Poly-Nag, a pseudonym for poly-N-acetylglucosamine. Options on the patents pertaining to cartilage have been taken by a major pharmaceutical firm, but those covering chitin[m] involving such things as chitin powders, creams and ointments, chitin-coated sutures, and chitin fiber nonwoven mats, are available for license. As with all food additives and medical substances to be inserted in the body, bandages or other preparations claiming a medicinal effect would have to be cleared with the Food and Drug Administration and this can be time-consuming and expensive. However, this burdensome task has already been partially completed in a four or five year program that has included long-term carcinogenicity tests and several investigational New Drug Applications.

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[k] A summary article appeared in Seminars on Arthritis and Rheumatism 3(4) pp. 287–321, Summer, 1974. Biological activity of bovine cartilage preparations. J.F. Prudden and Leslie Balassa.

[l] An additional 40 or 50 were obtained in foreign countries.

[m] U.S. Patents 3,632,754 3,914,413
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5 CONCLUSIONS ASPECTS WHICH MERIT FURTHER ACTION

5.1 Practical Options for Commercial Production and Utilization.

Our major conclusion is that it appears commercially feasible to produce between one and four million pounds of chitin/chitosan per year for sale at a price between $1.00 and $2.50 per pound. For both technical and economic reasons, the most effective business plan would be for certain strategically located shellfish (or food waste) processors to reduce shell waste to two dried components: (1) a mechanically separated protein for animal feed use and (2) a shell waste residual for sale to a regional or national chitin derivative producer. Such an arrangement would solve the garbage problem for many processors, probably at a reasonable profit when all credits are considered, without requiring them to enter fields far outside their present expertise. It would also provide a larger aggregate supply of chitinous shell residual to a chemical processor whose capabilities are more certain to include appropriate process, product, and market development capability.

Other options are possible, provided that both supply and marketing potentials are sufficiently assured. Thus, it is possible for an established seafood company, already in command of a substantial supply of waste, to process this material all the way to chitin or its derivatives, or for a chemical company (especially one with food chemical operations) to acquire a large and reliable supply of raw waste for conversion to sophisticated products. In both instances, some of the essentials related to supply control, economic stability, and product development or marketing capability are already present. However, at least one of these essentials would also require considerable development. The least efficient, most difficult, and certainly the most risky venture would be the creation of a completely independent enterprise to develop successfully or to control all of these essential functions from scratch.

While weighing the potentials for utilization of chitin, it is helpful to grade the prospective uses with respect to their technical and economic uncertainty. The least uncertainty attaches to applications already adopted, or having some significant development and evaluation behind them. Other applications, less well evaluated, are cited in Sections 5.2 and 5.3.

The principal market now being served, both here and in Japan, appears to be the application of chitosan as a coagulation aid for the settling and clarification of waste waters, as in the small sewage treatment plants mentioned in section 4.2.1. Similar applications presently active in Japan, but not yet in commercial use in this country, entail the removal of suspended solids from food processing waste water, or the conditioning of activated brewery or vegetable sludge. These applications are currently under study, and have successfully undergone some technical and economic evaluation in comparison with competing polymers.

Other applications with documented feasibility, but which are not yet commercial realities, are in the removal, separation, or collection of metal ions. Specifically, these include the removal from nuclear fuel solutions of radioactive elements that interfere with the determination of cesium,[1] the decontamination of atomic waste waters, the collection or preconcentration of zinc, copper, cadmium, or lead from sea water[2] or the collection or quantitative determination of mercury, vanadium or certain other metals in sea water or industrial brines.[3]

5.2 Promising Applications for Product and Process Development

In this section are grouped a number of suggested uses that are tentatively supported by a significant amount of experimental evidence, but that need specific development and detailed, comparative evaluation in at least one commercial application. Some of these, such as removal of mercury, chromium, or cyanide contaminants from wastes such as chloralkali brines or plating bath rinses, are analogous to the metal chelating applications cited in 5.1 above, but are contemplated on such large scale as to require critical cost-effectiveness comparisons with such potential competitors as dialdehyde starch, polyaminostyrene, or activated charcoal.

There is little doubt that chitin, or especially chitosan, would be useful in the battery of chromatographic supports generally maintained in a modern biochemical laboratory. However, pure and standardized products are required for this use, and some additional experience with chitin products in separating organic substances would be needed before market development could begin.

Wound treatments and coverings are similar in their requirement for high quality control and, despite an excellent experimental background, they need further evaluation, primarily in the attainment of FDA approval.

Paper additives are somewhat further from commercial development, in terms of the detailed information still required to evaluate cost effectiveness in such a large variety of potential uses. However, no one of these represents very much work or a very time-consuming or expensive prospect. Fiber recovery and the recovery of lignosulfonates are more speculative in terms of process development or commercial practicality.

5.3 Interesting Possibilities for Experimental Investigation or Exploration

A number of areas in chitin production and modification technology warrant further exploration. Alternative production chemistry appears to offer substantial rewards in cost saving, in the recovery or utilization of additional by-products, and probably in quality control, particularly for chitosan production. Chitin derivatives have only been superficially examined and their possibilities and properties could be beneficially extended and catalogued. Alternative sources, such as marine diatoms or cultured fungi, appear to have attractive potentials for increased or more efficient production of pure chitin or, in the case of *Mucor rouxii*, of chitosan.

Applications that are suggested by indirect evidence, but that have undergone little if any experimental testing as yet, include the development of surgical sutures, surgical accessories such as wound coverings, and medicament encapsulations.[a] As mentioned in section 4.2.3, these products are technically related to expertise employed in the development of meat casings, and investigators in any one of these areas should be alert to possible transfers of results.

Other areas in film technology that suggest good prospects are membranes whose performance depends on their inherent electric charge, such as the ion-exchange membranes needed for electrodialysis or desalination as described in section 2.3. Possibly other characteristics, such as spontaneous color changes in metal-chelating membranes, could be made useful, since they can be employed for visual estimation of chromate, copper, or molybdenum solutions down to 1 ppm or less.[4]

Finally, because of its strong but differentiated behavior with selected metals, for which it is already useful as an analytical tool, chitosan may allow development of advantageous methods of commercial separation or collection of metals. Perhaps some of the problems associated with separation of the components of marine manganese nodules may be reduced through utilization of this remarkable marine polymer. It would be an intellectually satisfying and logically appropriate closure of a great circle if the substance that may have been crucially instrumental in the original natural concentration of these ocean metals could be now exploited for their recovery by man.

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[a] Preliminary work on medicament carriers is described in U.S. Patent 3,911,098. Richard C. Capozza, assigned to American Cyanamid Company. Oct. 7, 1975.

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APPENDIX

TABLE 3.1a
Shellfish Landings, and Production of Processed Shellfish Products, 1972

	New England Fisheries									
	Maine		*New Hampshire*		*Massachusetts*		*Rhode Island*		*Connecticut*	
	Landings[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]
Blue Crab				*(has been included w/ Maine)*						*(has been included w/Rhode Island)*
Fresh & Frozen										
*Cooked Meat										
*Specialties										
Canned										
*Regular										
Stone Crab										
Cooked Claws										
Dungeness Crab										
Fresh & Frozen										
*Cooked Meat										
Cooked Whole										
*Specialties										
Canned										
*Regular										
King Crab										
Fresh & Frozen										
*Cooked Meat										
Rock Crab	754,000		22,000		47,000		349,000			
*Cooked Meat		*59,832*				[a]				
Cooked Whole						[a]				
*Specialties		[a]				[a]				
Snow Crab										
*Cooked Meat										
Sections										
Cooked Whole										
Canned										
*Regular										
Spiny Lobster										
Whole Cooked										
Tails Raw										
*Specialties										
Northern Lobster	16,257,000		674,000		8,032,000		3,361,000		540,000	
*Cooked Meat		*174,231*				*326,792*		*44,700*		
*Specialties		[a]						[a]		
Whole		105,000								
Crawfish										
*Cooked Meat										
*Specialites										
Shrimp	16,569,000		165,000		7,726,000					
Raw Headless		175,779								
*Peeled		*5,425,116*				*7,463,255*				
*Breaded		[a]				*1,163,273*				
*Specialties						*2,602,520*				
*Canned		[a]								
Cooked Whole		4,399,191				[a]				
Squid	2,000				688,000		750,000		6,000	
Frozen & Natural										
*Canned										
Total lbs processed		10,339,149				11,555,840		44,700		
Totals lbs processed w/ recoverable chitin		*5,659,179*				*11,555,840*		*44,700*		

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*Products processed in such a way as to furnish waste with potentially recoverable chitin are showin in italics.

[a] "Included with unclassified items"—presumably small

[b] Live weights (lbs)

[c] Processed product weight (lbs)

Source: Current Fishery Statistics Annual Summaries, NOAA, U.S. Dept. of Commerce

TABLE 3.1b
Shellfish Landings, and Production of Processed Shellfish Products, 1972

	Middle Atlantic Fisheries					
	New York		*New Jersey*		*Delaware & Pennsylvania*	
	Landings[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]
Blue Crab			1,437,000		2,552,000	
Fresh & Frozen						
**Cooked Meat*						
**Specialties*						*3,856,848*
Canned						
**Regular*				[a]		
Stone Crab						
Cooked Claws						
Dungeness Crab						
Fresh & Frozen						
**Cooked Meat*						
Cooked Whole						
**Specialties*						
Canned						
**Regular*						
King Crab						
Fresh & Frozen						
**Cooked Meat*		[a]				
Rock Crab			91,000			
**Cooked Meat*						
Cooked Whole						
**Specialties*						
Snow Crab						
**Cooked Meat*						
Sections						
Cooked Whole						
Canned						
Regular						
Spiny Lobster						
Whole Cooked						
Tails Raw						
**Specialties*						
Northern Lobster	1,145,000		1,308,000		22,000	
**Cooked Meat*				[a]		
**Specialties*				[a]		[a]
Crawfish						
**Cooked Meat*						
**Specialties*						
Shrimp			1,000			
Raw Headless						
**Peeled*		[a]				
**Breaded*		[a]				*354,651*
**Specialties*		[a]				[a]
**Canned*				[a]		
Squid	764,000		412,000			
Frozen & Natural		[a]				
**Canned*		[a]		[a]		
Totals lbs processed						4,211,499
Totals lbs processed w/ recoverable chitin						*4,211,499*

---

*Products processed in such a way as to furnish waste with potentially recoverable chitin are shown in italics.

[a] "Included with unclassified items"—presumably small

[b] Live weights (lbs)

[c] Processed product weight (lbs)

Source: Current Fishery Statistics Annual Summaries, NOAA, U.S. Dept. of Commerce

TABLE 3.1c
Shellfish Landings, and Production of Processed Shellfish Products, 1972

	Chesapeake Fisheries			
	Maryland		*Virginia*	
	Landings[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]
Blue Crab	23,482,000		48,554,000	
Fresh & Frozen				
*_Cooked Meat_		_2,968,044_		_3,440,019_
*_Specialties_		[a]		[a]
Canned				
*_Regular_				
*_Breaded_				
Meal		284,518		8,454,000
Stone Crab				
Cooked Claws				
Dungeness Crab				
Fresh & Frozen				
*_Cooked Meat_				
Cooked Whole				
*_Specialties_				
Canned				
*_Regular_				
King Crab				
Fresh & Frozen				
*_Cooked Meat_				
Rock Crab				
*_Cooked Meat_				
Cooked Whole				
*_Specialties_				
Snow Crab				
*_Cooked Meat_				
Sections				
Cooked Whole				
Canned				
*_Regular_				
Spiny Lobster				
Whole Cooked				
Tails Raw				
*_Specialties_				
Northern Lobster	21,000		884,000	
*_Cooked Meat_		[a]		
*_Specialties_				[a]
Crawfish				
*_Cooked Meat_				
*_Specialties_				
Shrimp				
Raw Headless				
*_Peeled_				
*_Breaded_				_182,480_
*_Specialties_		[a]		
*_Canned_		[a]		
Squid	4,000		262,000	
Frozen & Natural				
*_Canned_				
Total lbs processed		3,252,562		12,342,212
Total lbs processed w/ recoverable chitin		_2,968,044_		_3,888,212_

---

*Products processed in such a way as to furnish waste with potentially recoverable chitin are shown in italics.

[a] "Included with unclassified items"—presumably small

[b] Live weights (lbs)

[c] Processed product weight (lbs)

Source: Current Fishery Statistics Annual Summaries, NOAA, U.S. Dept. of Commerce

TABLE 3.1d
Shellfish Landings, and Production of Processed Shellfish Products, 1972

	South Atlantic Fisheries							
	North Carolina		*South Carolina*		*Georgia*		*Florida, East Coast*	
	Landings[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]
Blue Crab	13,479,000		7,422,000		9,059,000		6,288,000	
Fresh & Frozen								
**Cooked Meat*		*2,982,144*		*488,202*		*1,018,509*		*776,067*
**Specialties*		*102,622*		[a]		*902,498*		[a]
Canned								
**Regular*		[a]		[a]		[a]		[a]
Meal		5,346,000						
Stone Crab							67,000	
Cooked Claws								155,000
Dungeness Crab								
Fresh & Frozen								
**Cooked Meat*								
Cooked Whole								
**Specialties*								
Canned								
**Regular*								
King Crab								
Fresh & Frozen								
**Cooked Meat*								
Rock Crab								
**Cooked Meat*								
Cooked Whole								
**Specialties*								
Snow Crab								
**Cooked Meat*								
Sections								
Cooked Whole								
Canned								
**Regular*								
Spiny Lobster			165,000				6,268,000	
Whole Cooked								4,447,152
Tails Raw								1,775,195
**Specialties*								[a]
Northern Lobster								
**Cooked Meat*								
**Specialties*								
Crawfish								
**Cooked Meat*								
**Specialties*								
Shrimp	5,563,000		8,085,000		7,258,000		4,342,000	
Raw Headless		627,960				1,511,389		539,936
**Peeled*		[a]		*78,000*		*1,242,474*		
**Breaded*						*13,060,221*		*11,925,588*
**Specialties*		[a]						*443,494*
**Canned*		[a]		[a]				
Squid	15,000						8,000	
Frozen & Natural								
**Canned*								
Total lbs processed		9,058,726		566,202		17,735,091		20,062,432
Total lbs processed w/ recoverable chitin		*3,084,766*		*566,202*		*16,223,702*		*13,145,149*

*Products processed in such a way as to furnish waste with potentially recoverable chitin are shown in italics.

[a] "Included with unclassified items"—presumably small

[b] Live weights (lbs)

[c] Processed product weight (lbs)

Source: Current Fishery Statistics Annual Summaries, NOAA, U.S. Dept. of Commerce

TABLE 3.1e
Shellfish Landings, And Production of Processed Shellfish Products, 1972

	Gulf Fisheries									
	Florida-West		*Alabama*		*Mississippi*		*Louisiana*		*Texas*	
	Landings[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]
Blue Crab	10,673,000		1,613,000		1,362,000		15,185,000		6,464,000	
Fresh & Frozen										
**Cooked Meat*		*1,169,246*		*363,905*		*492,950*		*707,804*		*1,080,018*
**Specialties*		*322,385*		[a]				*700,397*		
Canned								[a]		
**Regular*						[a]				
Stone Crab	1,925,000									
Cooked Claws		30,283								
Dungeness Crab										
Fresh & Frozen										
**Cooked Meat*										
Cooked Whole										
**Specialties*										
Canned										
**Regular*										
King Crab										
Fresh & Frozen										
**Cooked Meat*										
Rock Crab										
**Cooked Meat*										
Cooked Whole										
**Specialties*										
Snow Crab										
**Cooked Meat*										
Sections										
Cooked Whole										
Canned										
**Regular*										
Spiny Lobster	5,149,000		39,000		191,000					
Whole Cooked		469,181								
Tails Raw		[a]								
**Specialties*										
Northern Lobster										
**Cooked Meat*										
**Specialties*										
Crawfish							2,505,000			
**Cooked Meat*								*9,209*		
**Specialties*								[a]		
Shrimp	22,828,000		17,549,000		7,951,000		83,035,000		97,578,000	
Raw Headless		5,385,956		12,881,977		5,057,000		24,595,835		38,903,687
**Peeled*		*10,194,544*[a]		*1,767,999*		[a]		*3,563,555*		*12,148,334*
**Breaded*		*32,492,435*						*2,176,868*		*26,859,742*
**Specialties*		[a]		[a]				*293,350*		
**Canned*						*2,301,588 lbs.*		*12,518,739 lbs.*		
**Other*								*8,819*		
Squid			4,000				[a]	595,434		
Frozen & Natural										
**Canned*										
Total lbs processed		50,064,040		15,013,881		7,851,538		45,170,016		78,991,781
Total lbs processed w/ recoverable chitin		*44,178,620*		*2,131,904*		*2,794,538*		*19,878,741*		*40,088,094*

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*Products processed in such a way as to furnish waste with potentially recoverable chitin are shown in italics.

[a] "Included with unclassified items"—presumably small

[b] Live weights (lbs)

[c] Processed product weight (lbs)

Source: Current Fishery Statistics Annual Summaries, NOAA, U.S. Dept. of Commerce

TABLE 3.1f
Shellfish Landing, And Production of Processed Shellfish Products, 1972

Pacific Coast and Hawaii Fisheries

	Alaska		*Washington*		*Oregon*		*California*		*Hawaii*	
	Landings[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]	*Landings*[b]	*Processed*[c]
Blue Crab									112,910	
Fresh & Frozen										
**Cooked Meat*										
**Specialties*										
Canned										
**Regular*										
Stone Crab										
Cooked Claws										
Dungeness Crab	7,540,000		12,382,000		6,762,000		1,563,000			
Fresh & Frozen										
**Cooked Meat*		*48,372*		*1,478,480*		*969,166*		*529,218*		
Cooked Whole		2,619,434 +				121,166				
**Specialties*		*957,654 sections								
Canned										
**Regular*		*30,503*		*2,747*						
King Crab	94,245,000									
Fresh & Frozen										
**Cooked Meat*		*9,802,893*								
Whole & Sections										
**Canned*		8,964,659								
Rock Crab		*316,811*					843,000			
**Cooked Meat*										
Cooked Whole										
**Specialties*										
Snow Crab	46,010,000									
**Cooked Meat*		*2,974,235*								
Sections		2,831,083								
Cooked Whole		1,002,735								
Canned										
**Regular*		*160,069*								
Spiny Lobster							398,000		5,195	
Whole Cooked										
Tails Raw										
**Specialties*										
Northern Lobster										
**Cooked Meat*										
**Specialties*										
Crawfish			7,000		9,000		73,000			
**Cooked Meat*										
**Specialties*										
Shrimp	83,826,000		1,670,000		20,741,000		2,907,000		1,077	
Raw Headless		2,629,190								
**Peeled*		*2,486,675*				*2,853,501*		*2,194,671*		
**Breaded*				*125,133*				*8,839,274*		
**Specialties*		*7,678,665*		*1,296,013*						
**Canned*										
Sections		2,803,287					20,159,000		2,240	
Squid								5,441,136		
Frozen & Natural										
**Canned*										
Total lbs processed		45,306,265		2,902,373		3,943,833		17,004,299		[a]
Total lbs processed w/ recoverable chitin		*23,498,223*		*2,902,373*		*3,943,833*		*11,563,163*		

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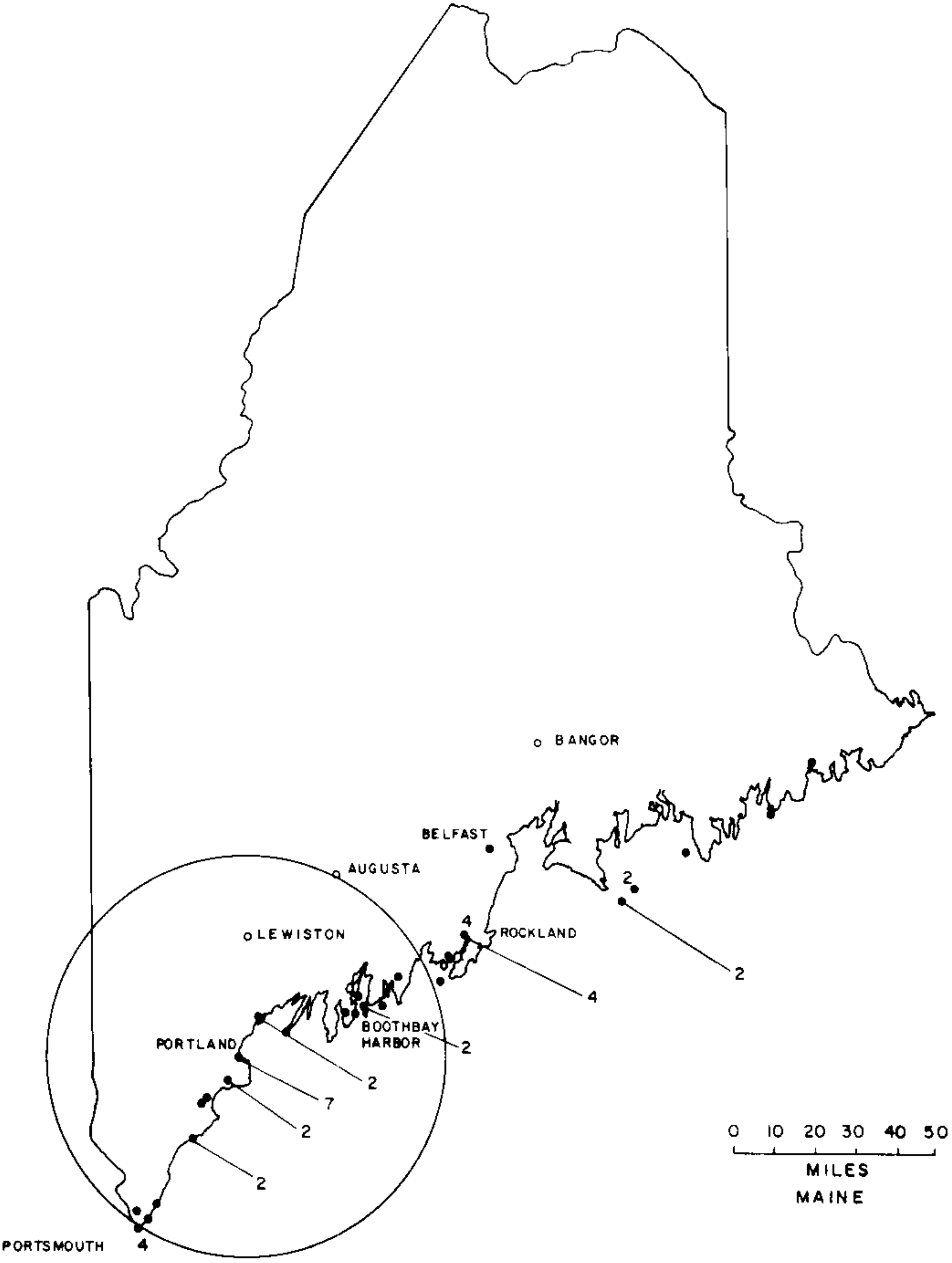
*Products processed in such a way as to furnish waste with potentially recoverable chitin are shown in italics.

[a] "Included with unclassified items"—presumably small

[b] Live weights (lbs)

[c] Processed product weight (lbs)

Source: Current Fishery Statistics Annual Summaries, NOAA, U.S. Dept. of Commerce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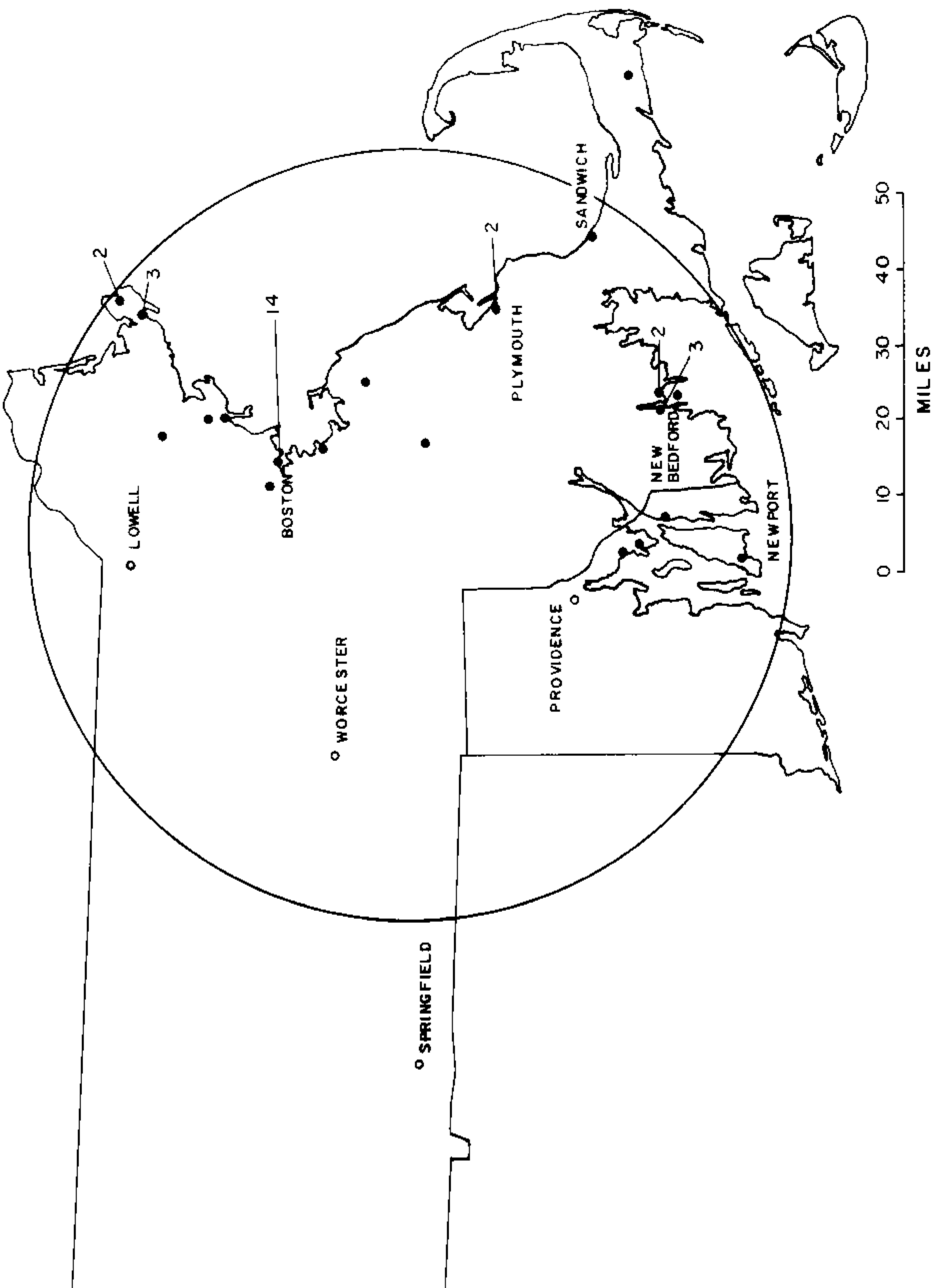

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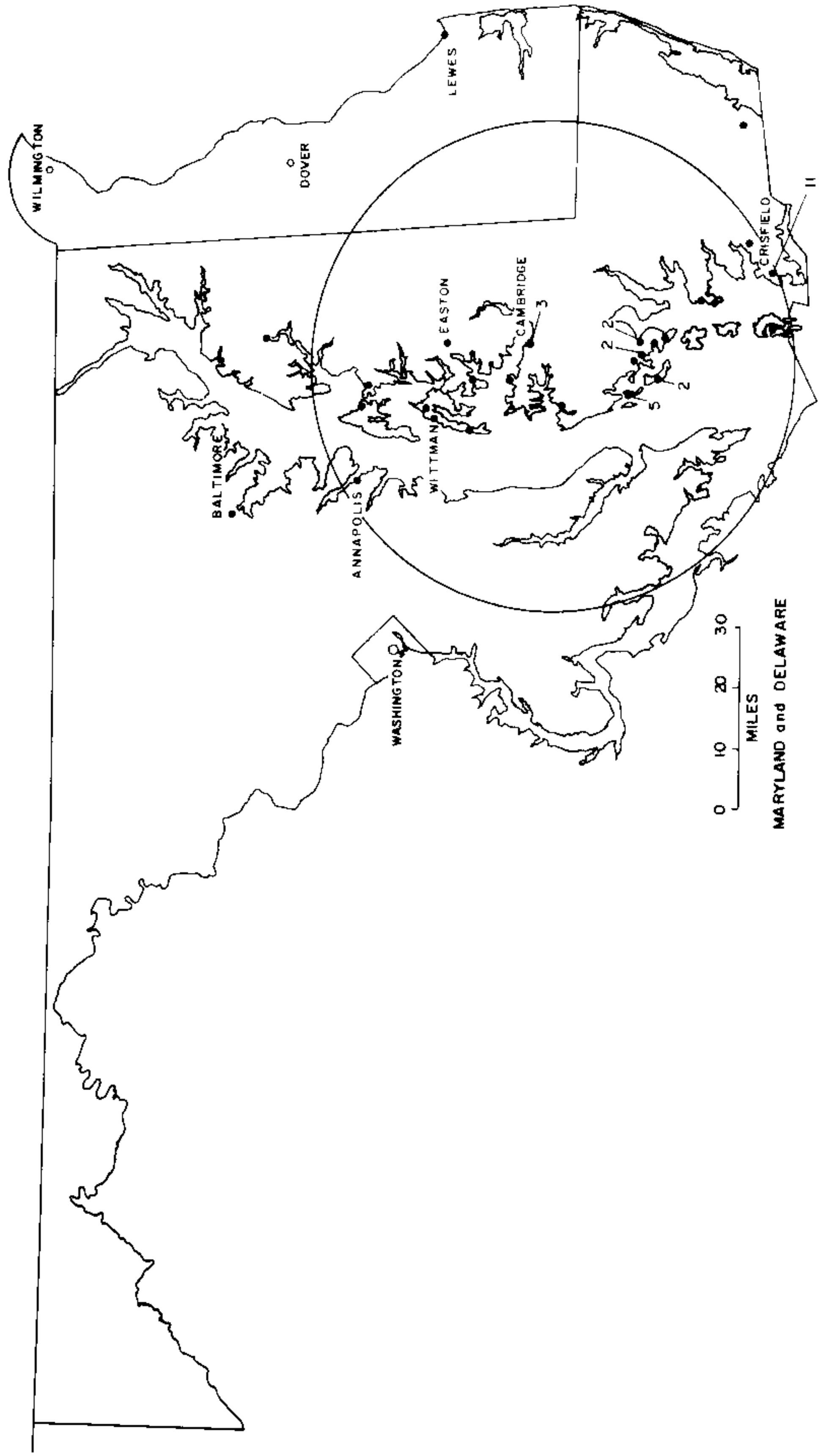
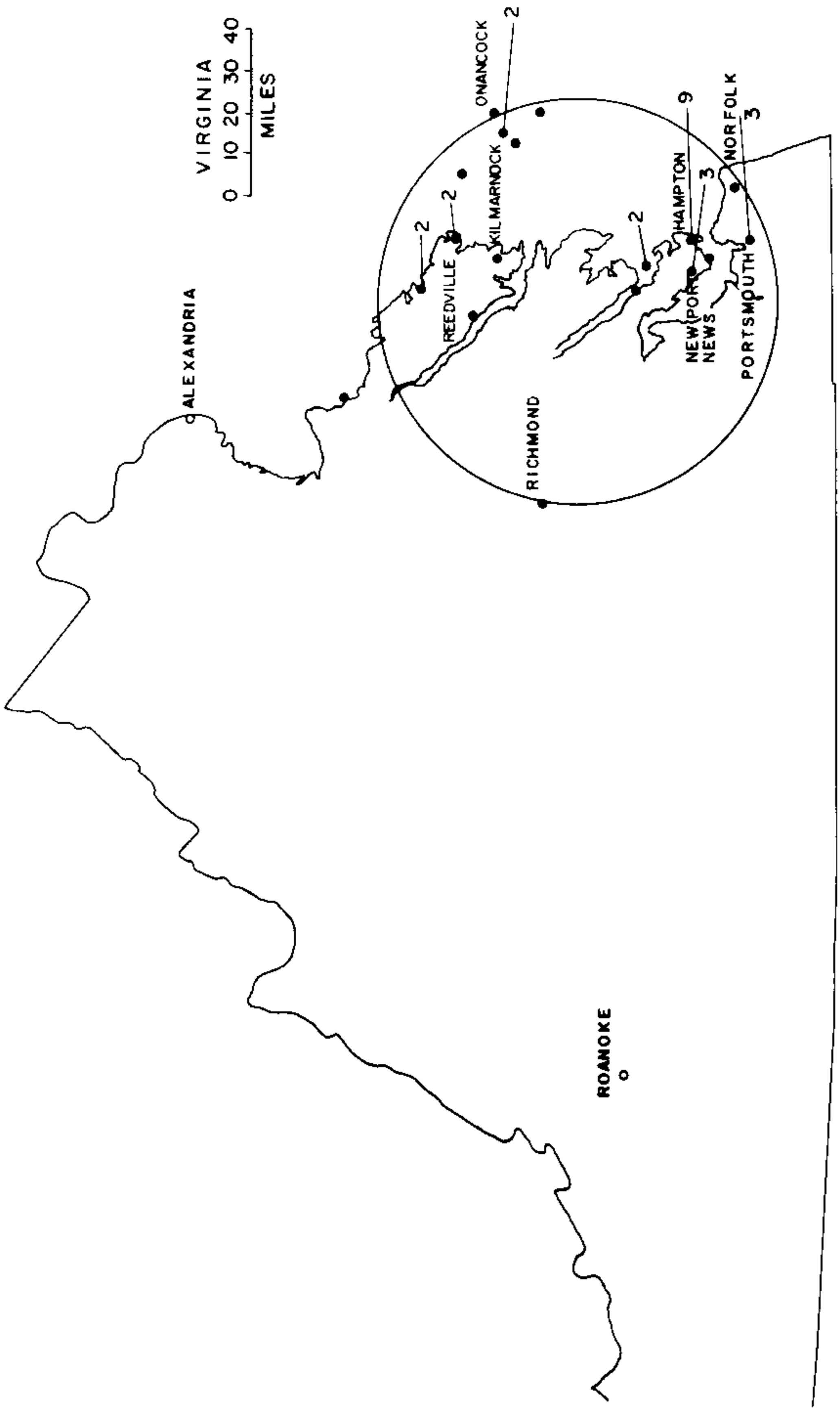


MARYLAND and DELAWARE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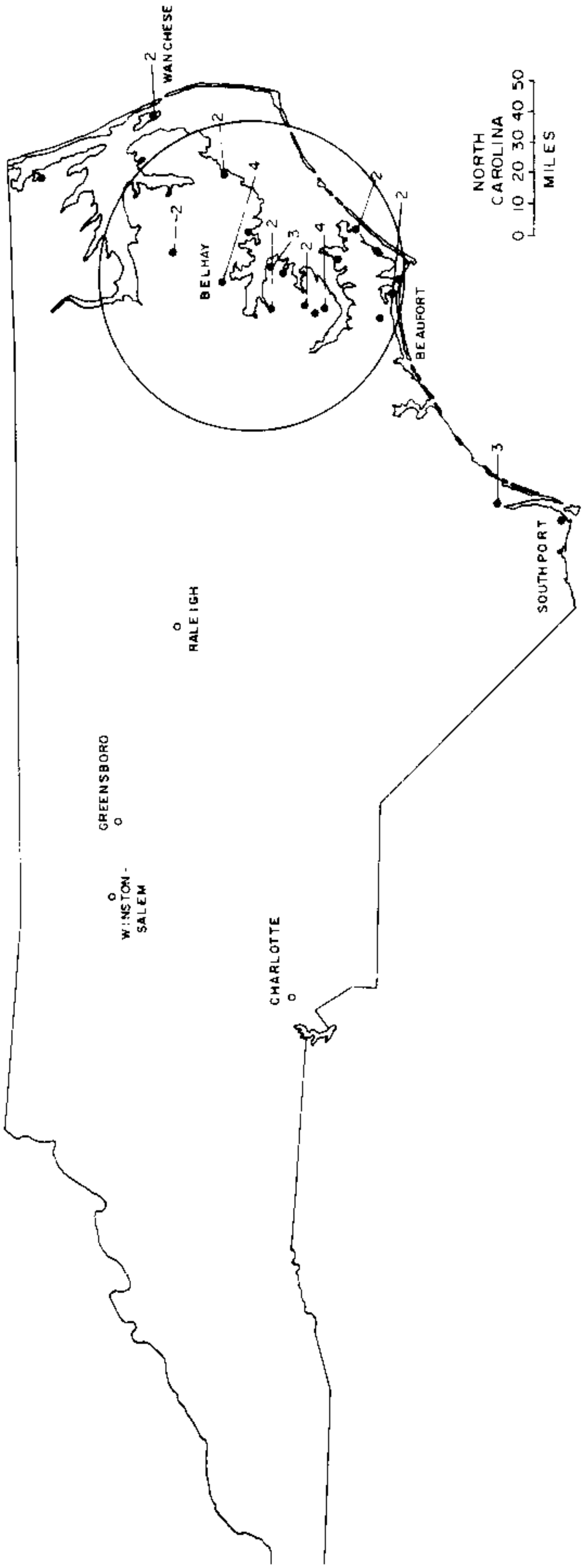
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BEAUFORT
SOUTHPORT
RALEIGH
GREENSBORO
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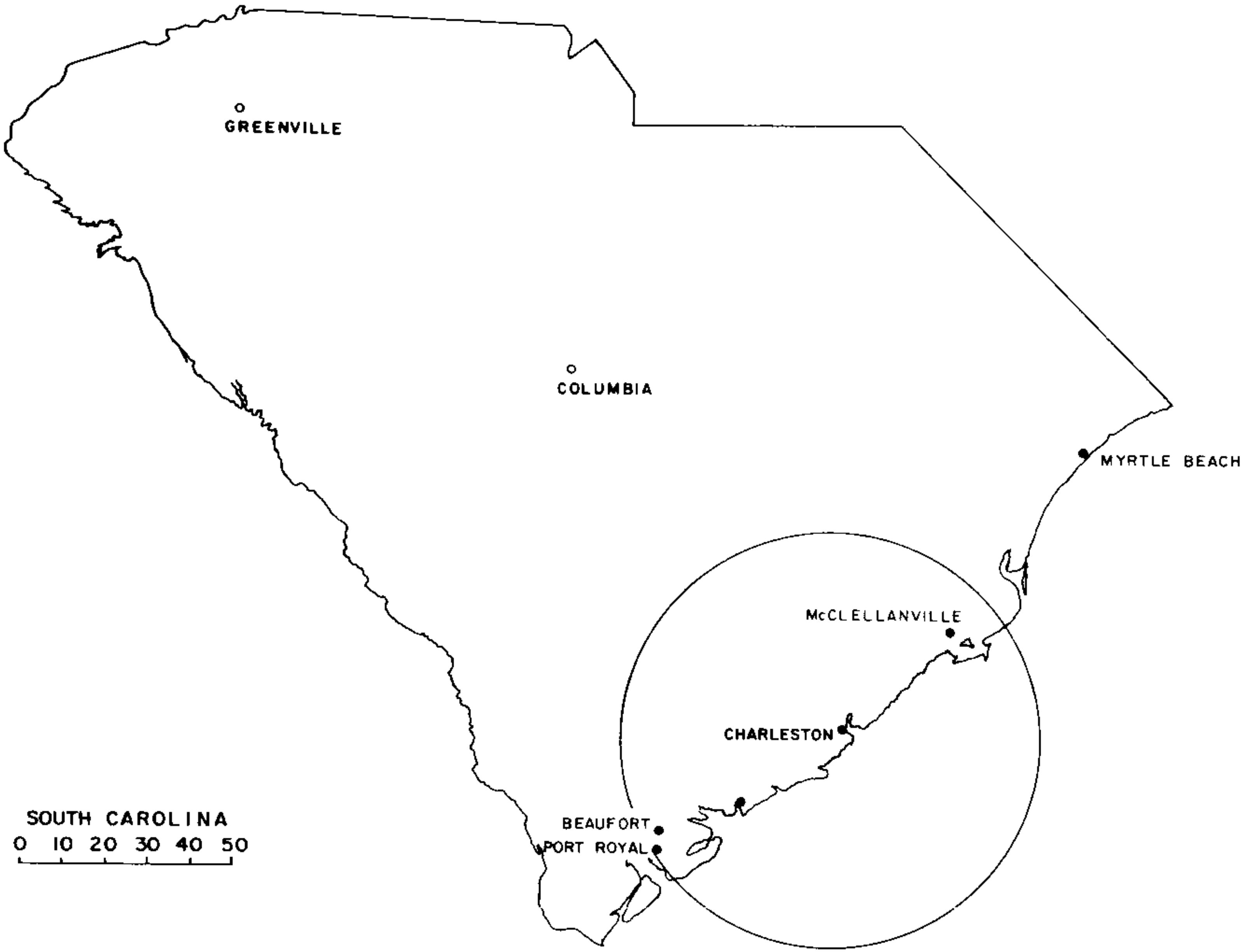
3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MYRTLE BEACH
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PORT ROYAL
SOUTH CAROLINA
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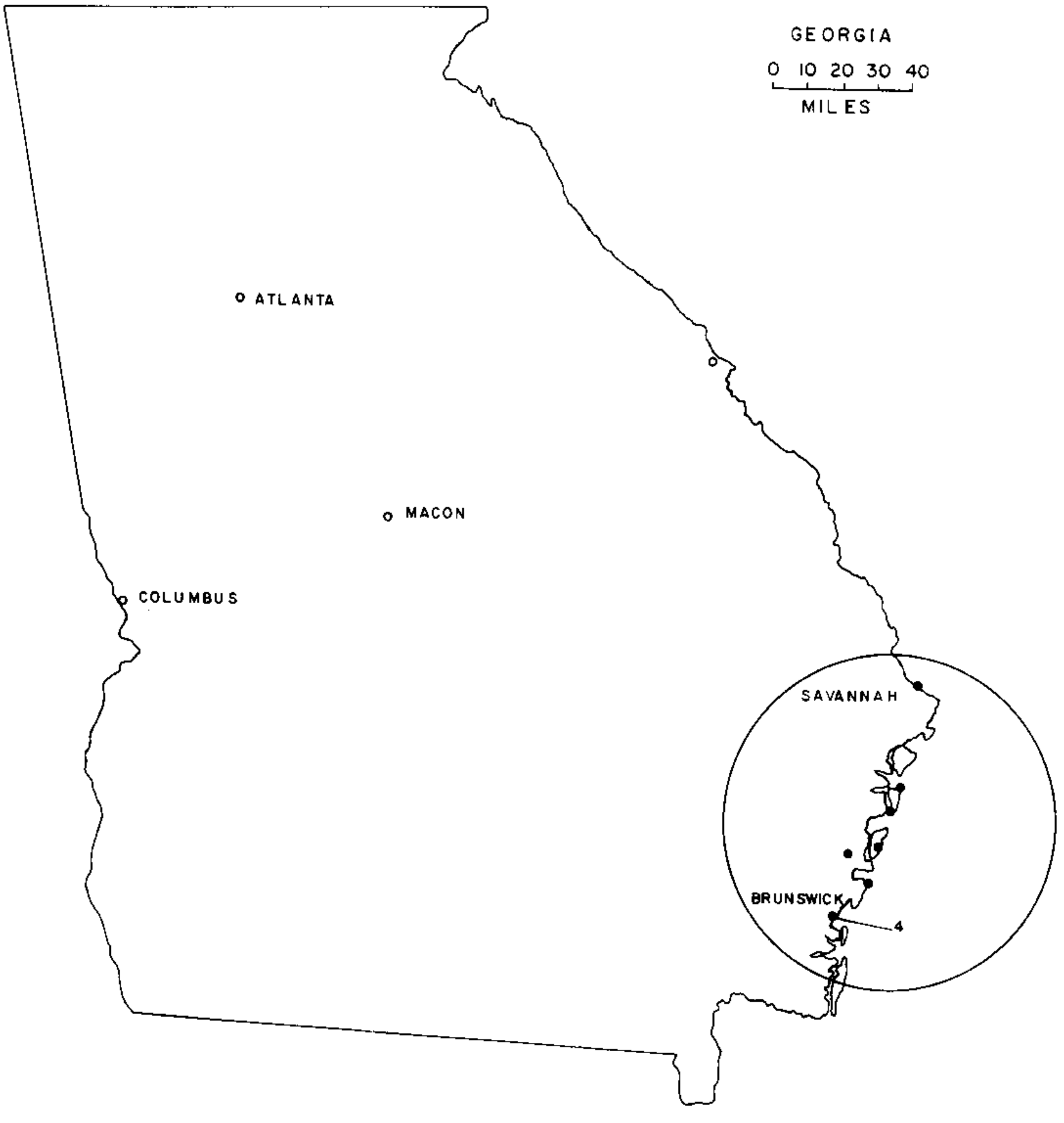
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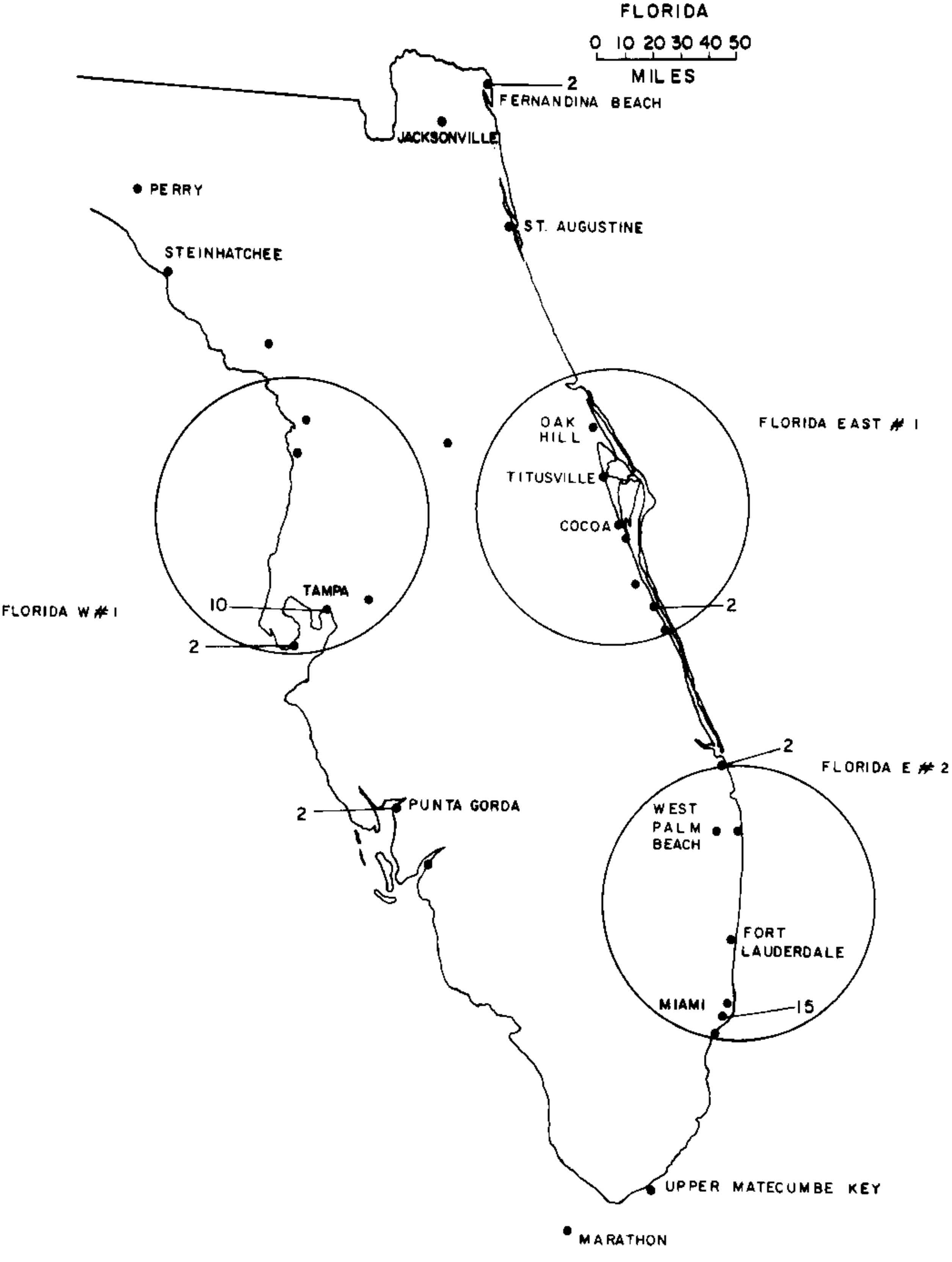
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OAK HILL
TITUSVILLE
COCOA
TAMPA
10
FLORIDA W # 1
2
2
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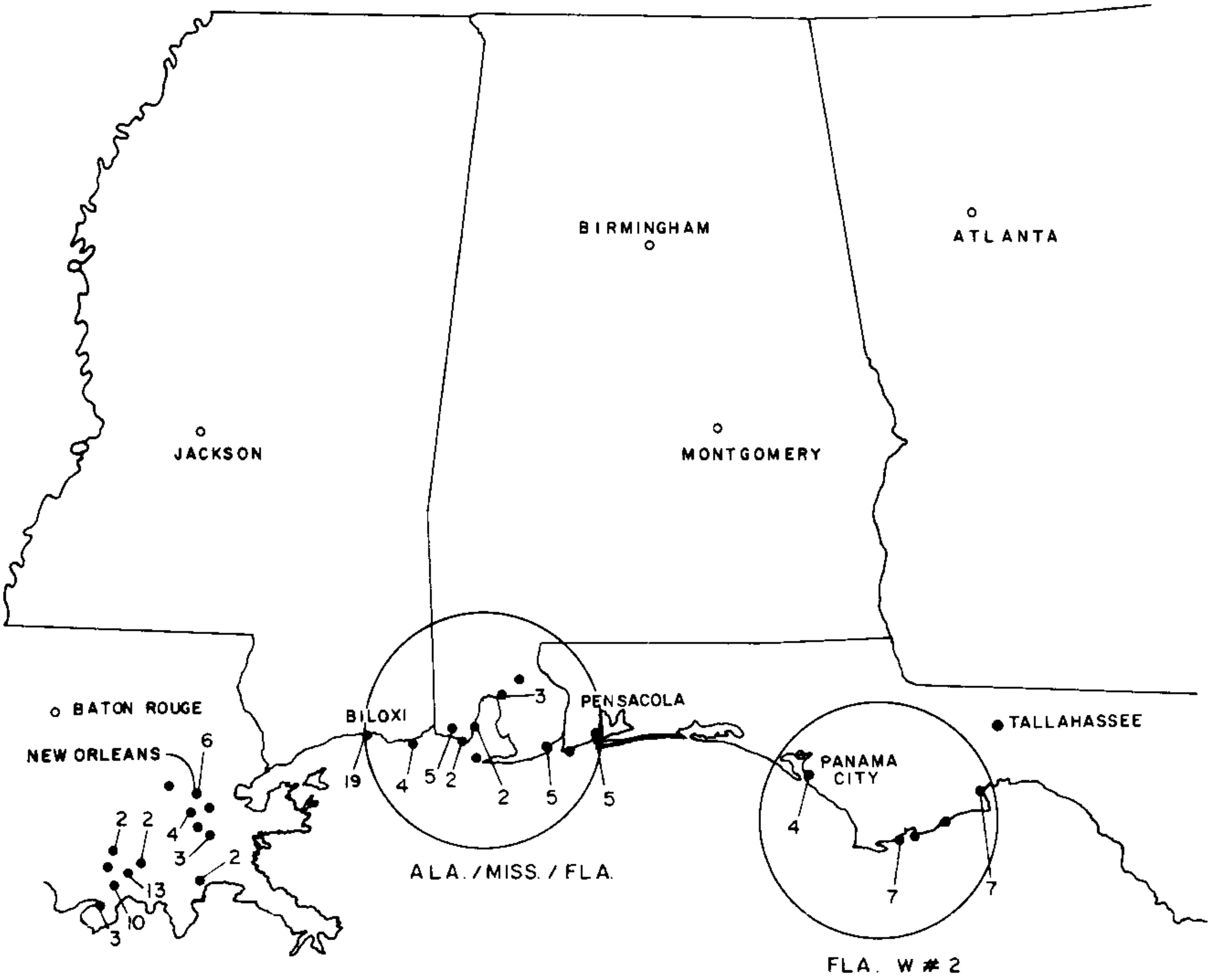
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TALLAHASSEE
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6
2
2
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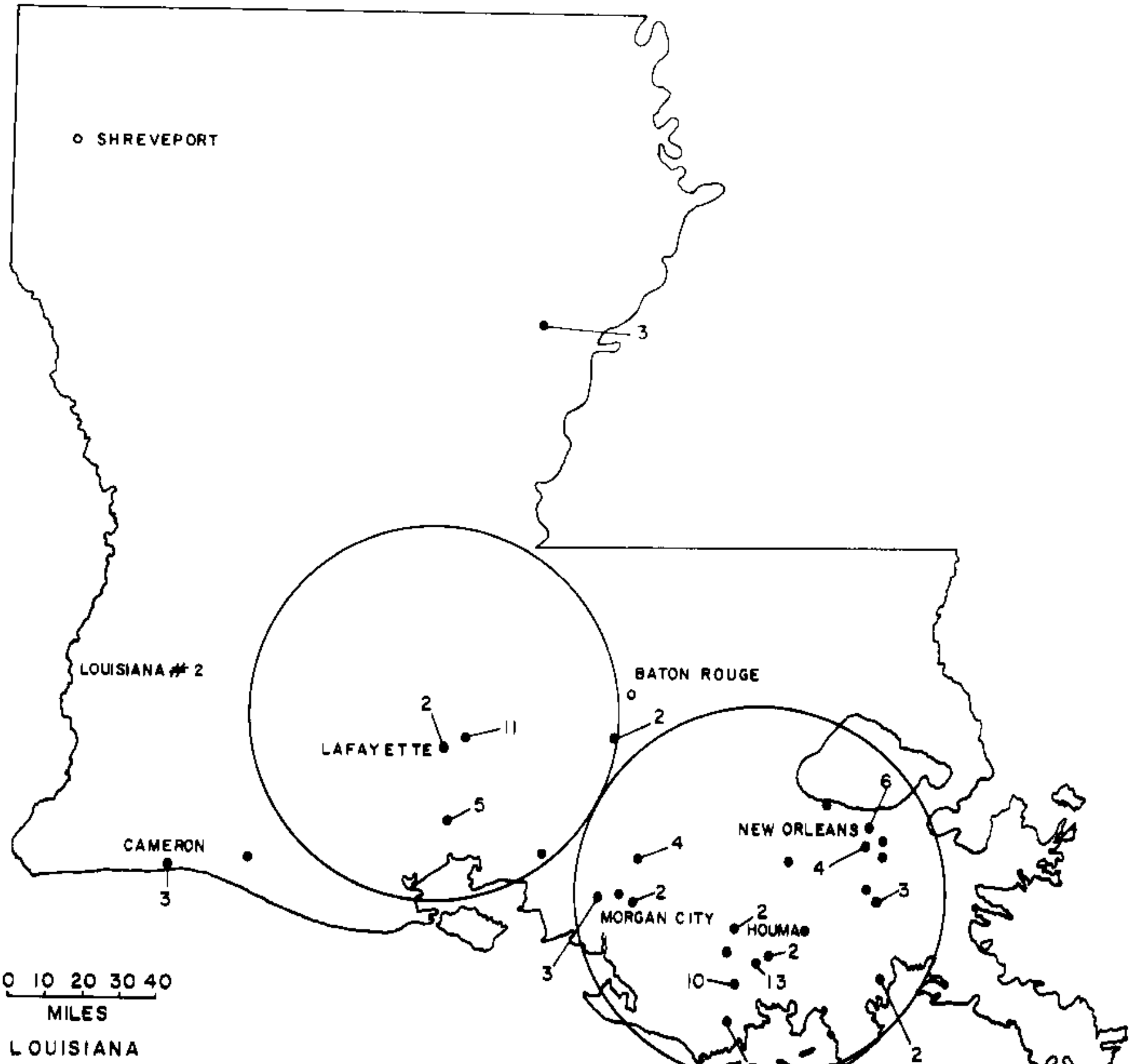
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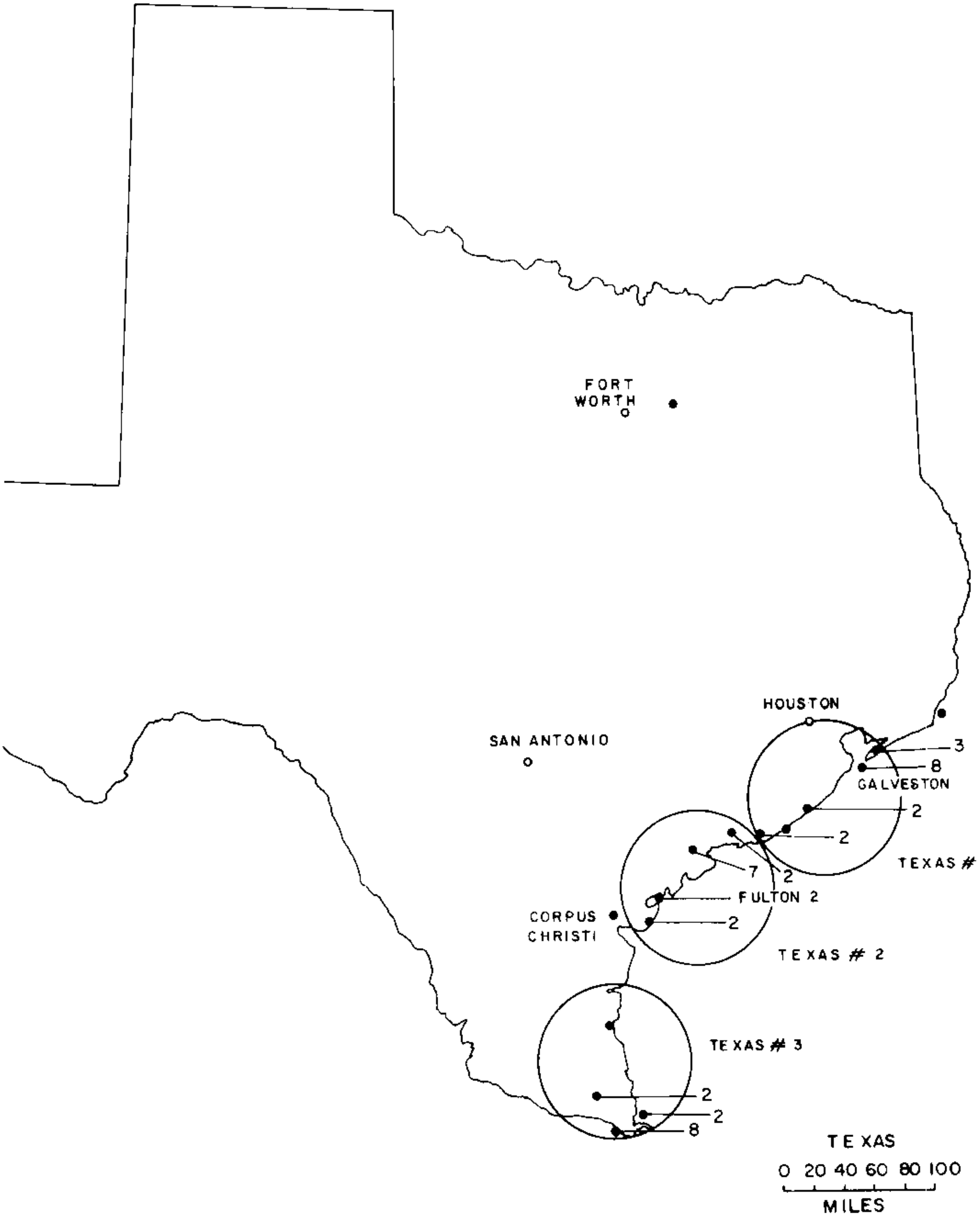
LOUISIANA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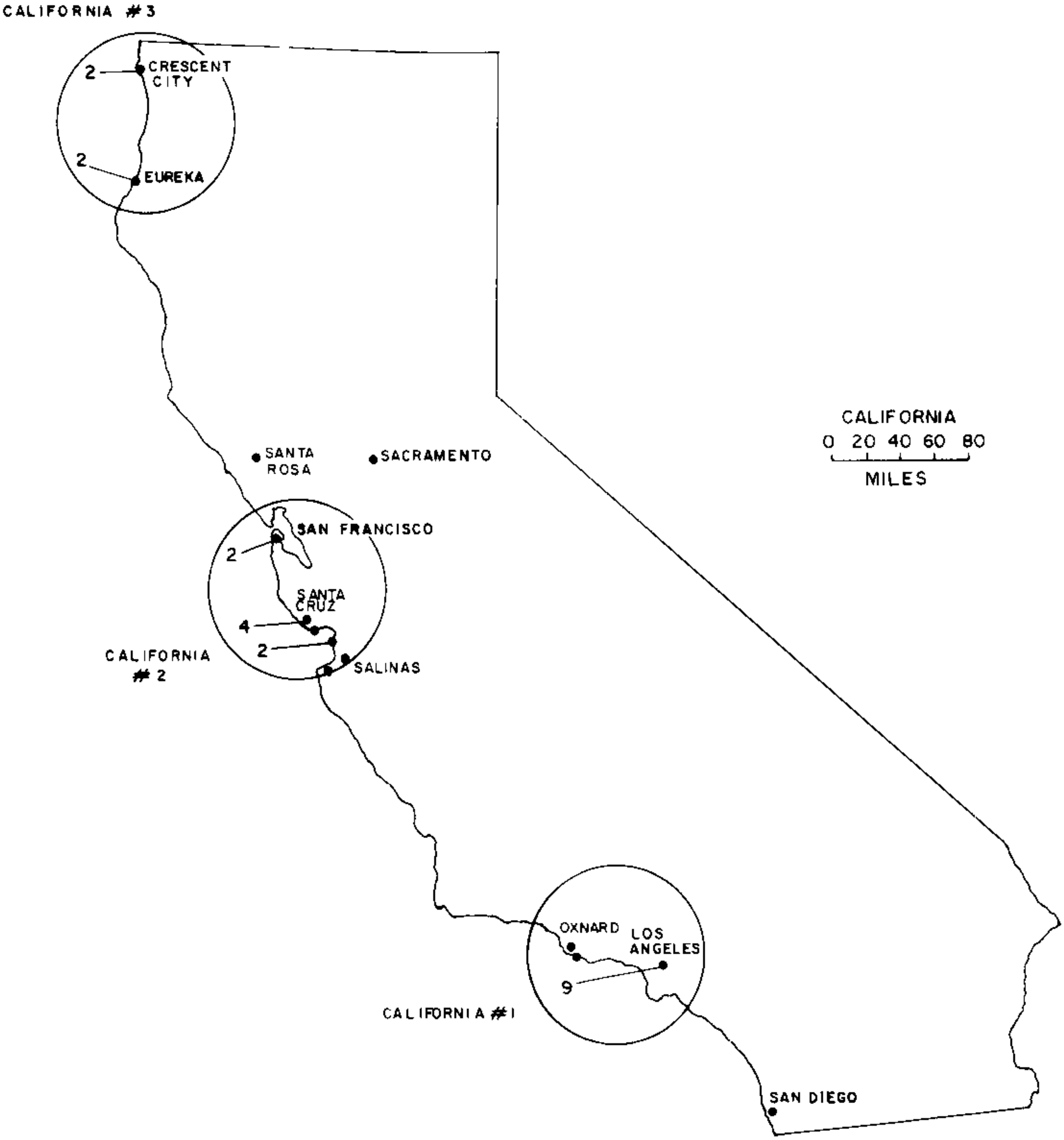
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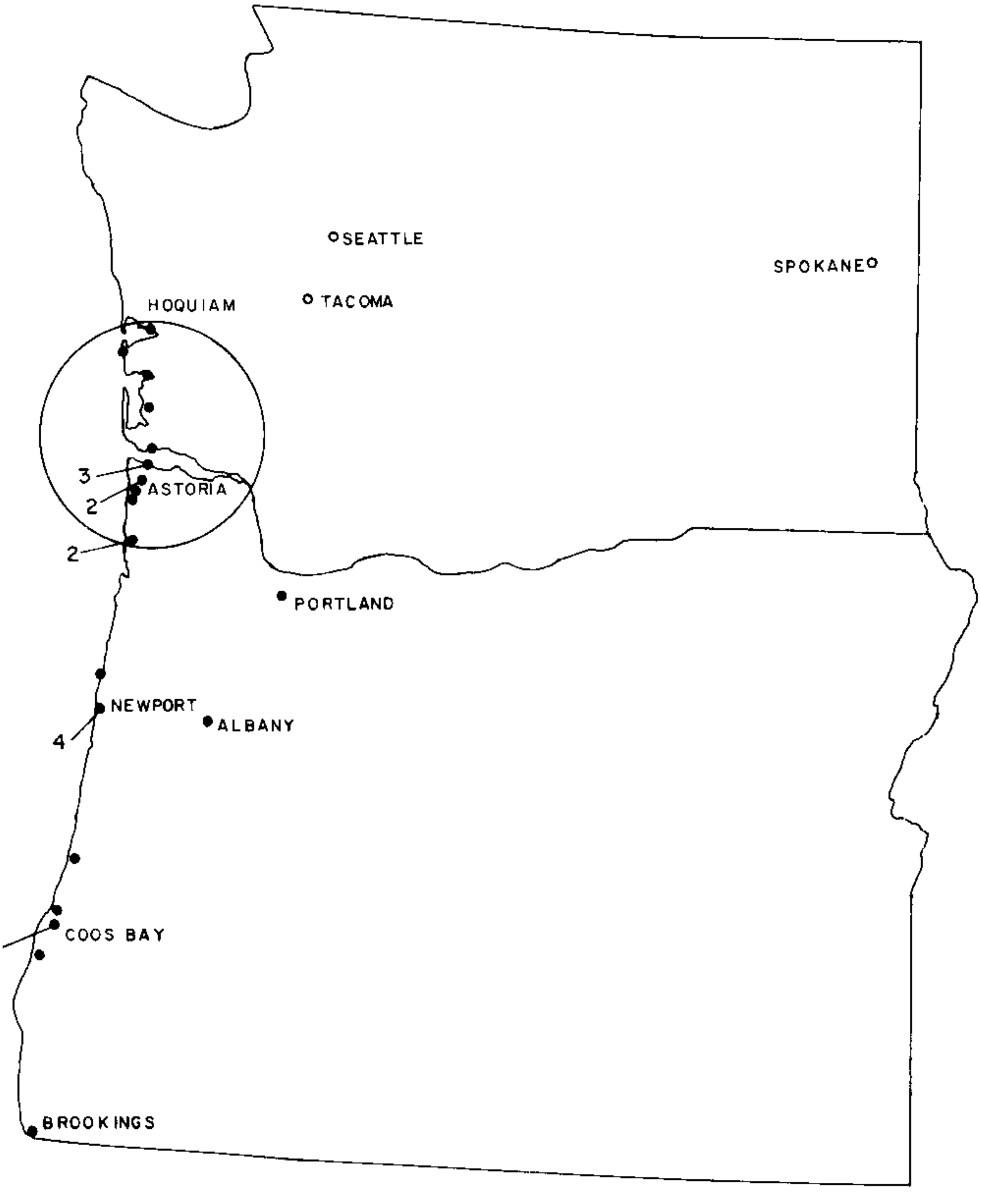
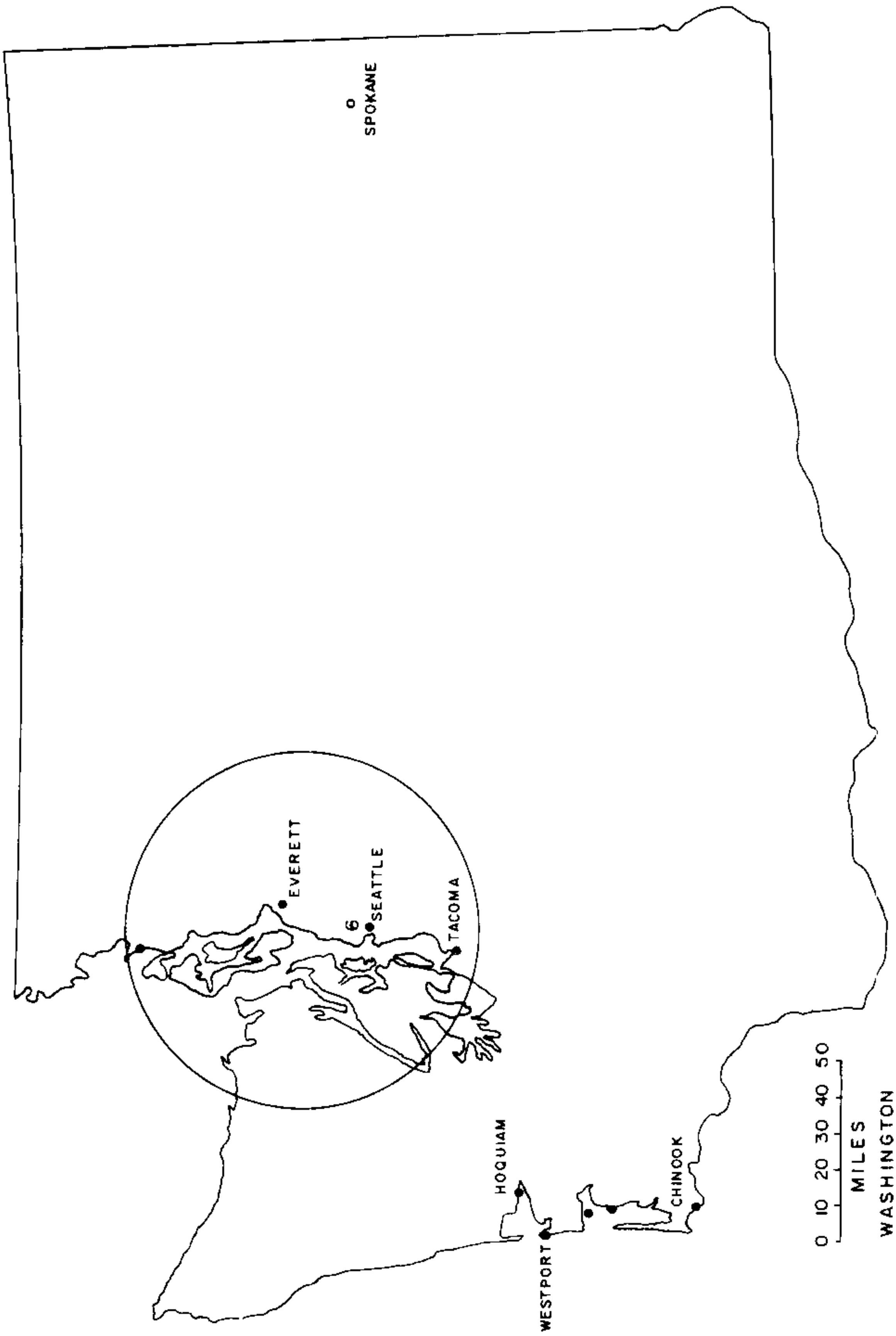
SAN DIEGO



WASHINGTON — OREGON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