REFERENCES

- Agemian, H. 1997. Determination of nutrients in aquatic sediments. In A. Mudroch,

 J. M. Azcue and P. Mudroch(eds.), Manual of Physico-Chemical Analysis of

 Aquatic sediments, pp. 215-218. New York: Lewis Publishers.
- Aspila, K. I., Ageman, H. and Chau, A.S.Y. 1976. A semi-automatic method for the determination of inorganic, organic and total phosphate in sediments. <u>Analyst</u> 101: 187-197.
- Balchand, A. N. and Nair, S. M. 1994. Fractionation of phosphorus in the sediments of a tropical estuary. <u>Environmental Geology</u> 23: 284-294.
- Barbanti, A. Bergamini M. C., Frascari, F., Miserocci, S. and Rosso, G. 1994. Critical aspects of sedimentary phosphorus chemical fractionation. <u>Journal of Environmental Quality</u> 23(5): 1093-1102.
- Baturin, G. N. 1988. Disseminated phosphorus in oceanic sediments- a review. Marine Geology 84: 95-104.
- Berner, R. A., Ruttenberg, K. C., Ingall, E. D. and Rao, J. L. 1993. The nature of phosphorus burial in modern marine sediments. In R. Wallast, F. T. Mackenzie and L. Chou (eds.), Interactions of C, N, P and S Biogeochemical Cycles and Global Change, pp.365-378. Berlin Heidelberg: Springer-Verlag.
- Blomqvist, S., Hjellstrom, K., Sjosten, A. 1993. Interference from arsenate, fluoride and silicate when determining phosphate in water by the phosphoantimonyl-molybdenum blue method. <u>International Journal of Environmental Analytical Chemistry</u> 54(1): 31-43.
- Bostrom, B. 1984. Potential mobility of phosphorus in different types of lake sediments.

 Hydrobiologia 69: 457-474.
- Bostrom, B., Ahlgren, I. And Bell. R. 1985. Internal nutrient loading in a eutrophic lake, reflect in seasonal variations of some sediment parameters. <u>Vehr. Int. Ver. Limnol.</u> 18: 5-59.
- Butler, E. E. and Tibbits, S. 1972. Chemical survey of the Tamar Estuary. 1. Properties of the waters. J. Mar. Biol. Assoc. U.K. 52: 681-699.

- Carritt, D. E. and Goodgal, S. 1954. Sorption reaction and some ecological implications.

 Deep-Sea Res. 1: 224-243.
- Chambers, R. M., Fourqurean, J. W., Hollibaugh, J. T. and Vink. S. M. 1995. Importance of Terresitrially-Derived, Particulate Phosphorus to Phosphorus Dynamics in a West Coast Estuary. <u>Estuaries</u> 18(3): 518-526.
- Chang, S. C. and Jackson, M. L. 1957. Fractionation of Soil Phosphorus. <u>Soil Science</u> 84: 133-144.
- Chang, S. C. and Jackson, M. L. 1958. Soil phosphorus fractionation in some representative soils. <u>Journal of Soil Science</u> 9(1): 109-119.
- Chase, E. M. and Sayles, F. L. 1980. Phosphorus in Suspended Sediments of the Amazon River. Estuarine and Coastal Marine Science 11: 383-391.
- Compton, J., Mallinson, D., Glenn, C. R., Foellmi, K., Shields, G. and Zanin, Y. 2000.

 Variation in the global phosphorus cycle. Marine Authigenesis: From Global to

 Microbial SEPM Special Publications No. 66. 21-33.
- Conley, D. J., Smith, W.M. Cornwell, J. C. and Fisher, T. R. 1995. Transformation of Particle-bound Phosphorus at the Land-Sea Interface. <u>Estuarine Coastal and Shelf Science</u> 40: 161-176.
- De Groot, C. J. 1990. Some remarks on the presence of organic phosphates in sediments. Hydrobiologia 207: 303-309.
- De Groot, C. J. and Golterman, H. L. 1990. Sequential fractionation of sediment phosphate. <u>Hydrobiologia</u> 192:143-149.
- De Groot, C. J. and Golterman, H. L. 1993. On the presence of organic phosphate in some Camargue sediments: evidence for the importance of phytate.

 Hydrobiologia 252: 117-126.
- Delaney, M. L. and Anderson L. D. 1997. Phosphorus Geochemistry in Ceara Rise Sediments. In N.J. Shackleton, W.B. Curry, C. Richter and T.J. Bralower (eds.), Proceedings of the Ocean Drilling Program, Scientific Results, 154: 475-481.
- Dutro, J.T., Dietrich, R.V. and Foose, R.M., comps. 1989. <u>AGT datasheets: for geology in the field, laboratory, and office</u>. 3 rd ed. Virginia: United Book Press.

- Eijsink, L. M., Krom, M. D. and de Lange, G. J. 1997. The use of sequential extraction techniques for sedimentary phosphorus in eastern Mediterranean sediments.

 Marine Geology 13: 147-155.
- Eyre, B. and Mcconchie, D. 1993. Implication of sedimentological studies for environmental pollution assessment and management-examples from fluvial systems in North Queensland and Western Australia. <u>Sedimentary Geology</u> 85:1-4.
- Filippelli, G. M. and Ruttenberg, K. C. 1997. Preface: Phosphorus Cycling and Sedimentation in Marine and Freshwater System. Marine Geology 139: 1-4.
- Förstner, U. and Wittmann, G.T.W. 1981. Metal Pollution in the Aquatic Environment.

 Heidelberg: Springer-verlag.
- Fox, L.E. 1989. A model for inorganic control of phosphate concentrations in river waters. Geochim. Cosmochim. Acta 53: 417-428.
- Fox, L. E., Sager, S. L. and Wofsy, S. C. 1985. Factors controlling the concentration of soluble phosphorus in the Mississippi Estuary. <u>Limnol. Oceanogr.</u> 30: 826-832.
- Fox, L. E., Sager, S. L. and Wofsy, S. C. 1986. The chemical control of soluble phosphorus in the Amazon River and Estuary. <u>Geochim. Cosmochim. Acta</u> 50: 783-794.
- Froelich, P. N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. <u>Limnol. Oceanogr.</u> 33: 849-668.
- Froelich, P.N., Bender, M.L., Luedtke, N.A. Health, G.R. and DeVries, T., 1982. The marine phosphorus cycle. <u>Am. J. Sci.</u> 282: 474-511.
- Golterman, H. L., 1984. Sediments, modifying and equilibrating factors in the chemistry of fresh waters. <u>Verh. Int. Ver. Limnol.</u> 22: 23-59.
- Golterman, H. L. and Booman, A. 1988. Sequential extraction of iron-phosphate and calcium phosphate from sediments by chelating agents. <u>Verh. Int. Ver. Limnol.</u> 23: 904-909.
- Grosline, D.S. 1960. A lecture at University of Texas, Austin.

- Gross, M.G. 1971. Carbon determination. In Carver, R. E. (ed.), <u>Procedure in sedimentary Petrology</u>, pp.571-636. USA:Wiley-Interscience.
- Haunxin, W., Presley, B. J., Velinsky, D. J. 1997. Distribution and sources of phosphorus in tidal rivers sediments in the Washington, D.C., Area. <u>Environmental Geology</u> 30: 224-230.
- Hieljes, A.H.M. and Liklema, L. 1980. Fractionation of inorganic phosphates in calcarous sediments. <u>J. Environ. Qual.</u> 9: 405-407.
- Horne, A.J. and Goldman, C.R. 1994. Limnology. 2nd ed. Singapore: McGraw-Hill.
- Jensen H.S. and Thamdrup, B. 1993. Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. <u>Hydrobiologia</u> 253(1-3): 47-59.
- Krauskopf, K.B. 1989. <u>Introduction to Geochemistry</u>. <u>International edition 4th ed.</u>
 Singapore: McGraw-Hill.
- Krom, M. D., Kress, N., Brenner, S. and Gordon, L. I. 1991. Phosphorus limitation of primary productivity in the eastern Mediterranean Sea. <u>Limnol. Oceanogr.</u> 36: 424-432.
- Lebo, M. E. 1991. Particle-bound phosphorus along an urbanized coastal plain estuary.

 Marine chemistry 34: 225-246.
- Liss, P. S. 1976. Conservative and non-conservative behavior of dissolved constituents during estuarine mixing. In J.D. Burton and P.S. Liss (eds.), Estuarine Chemistry, pp. 93-130. New York: Academic Press.
- Loring, D. H. and Rantala, R. T. T. 1977. Geochemical analyses of marine sediments and suspended particulate matter. <u>Fisheries and Marine Services, Canada Technical Report</u> 700: 58.
- Lucotte, M. and D' Anglejan, B. 1983. Forms of phosphorus and phosphorus iron relationship in the suspended matter of the St. Lawrence Estuary. <u>Canadian</u>

 Journal of Earth Science 20:1880-1890.
- Lucotte, M. and B. D' Anglejan. 1985. A comparison of several method for the determination of iron hydroxides and associated orthophosphates in estuarine particulate matter. <u>Chem.Geol.</u> 48: 257-264.

- Martin, D. F. 1970. Marine Chemistry volume 2 Theory and Applications, pp. 183-223.

 New York: Marcel Dekker.
- Martin, J.M., P. Nirel, And A.J. Thomas. 1987. Sequential extraction techniques, promises and problems. <u>Marine Chemistry</u> 22: 313-341.
- Moody, J.B. Chaboudy, L.D. and Worsley T.R. 1988. Pacific pelagic phosphorus accumulation during the last 10 M.Y. <u>Paleoceanography</u> 3: 113-136.
- Morris, A. W., Bale, A. J. and Howland, R. J. M. 1981. Nutrient distribution in an estuary: Evidence of chemical precipitation of silicate and phosphate.

 Estuarine Coastal and Shelf Science 12: 205-216.
- Mortimer, C.H. 1971. Chemical exchange between sediments and water in great lakesspeculation on probable regulartory mechanisms. <u>Limnol. Oceanogr</u>. 16: 387-404.
- Palmer, M.R. 1985. Rare earth elements in feraminifera tests. <u>Earth and Planetary</u>
 <u>Science Letters</u>, 73: 285-298.
- Pardo, P., Lopez-Sanchez, J.F., and Rauret, G. 1998. Characterisation, validation and comparison of three methods for the extraction of phosphate from sediments.

 <u>Analytica Chimica Acta</u> 376:183-195.
- Pardo, P., Lopez-Sanchez, J.F., Rauret, G., Ruban, V., Muntau, H. and Quevauviller, P.1999. Study of the stability of extractable phosphate content in a candidate reference material using a modified William's extraction procedure. <u>Analyst</u> 124: 407-411.
- Pomeroy, L.R., Smith, E. E. and Grant, C. M. 1965. The exchange of phosphate between estuarine waters and sediments. <u>Limnol. Oceanogr.</u> 10: 167-172.
- Prapong, P. 1992. <u>Behaviour of Nutrient in Tha-Chin Estuary</u>. Master's Thesis, Interdepartment of Environmental Sciences, Graduate School, Chulalongkorn University.
- Psenner, R. Bostrom, B., Dinka, M., Petterson, K., Pucsko, R. and Sager, M. 1988.

 Fractionation of phosphorus in suspended matter and sediment. <u>Ergeb. Limnol.</u>
 30: 98-113.

- Ruban, V. Lopez-Sanchez, J.F., Pardo, P. Rauret, G., Muntau, H. and Quevauviller, P.H. 1999. Selection and evaluation of sequential extraction procedures for the determination of phosphorus forms in lake sediment. <u>J. Environ. Monit.</u> 1: 51-56.
- Ruttenberg, K. C. 1992. Development of sequential extraction method for different forms of phosphorus in marine sediments. <u>Limnol. Oceanogr.</u> 37: 1460-1482.
- Ruttenberg, K.C. and Berner, R.A. 1993. Authigenic apatite formation and burial in sediments from non-upwelling continental margin environments. <u>Geochim. Cosmochim. Acta</u> 57: 991-1007.
- Shapiro, L. 1967. Rapid analysis of rocks and minerals by a single-solution method.

 U.S. Geol. Surv. Prof. Pap. 575-B 187-191.
- Sharp, J. H., Culberson, C. H. and Church, C. M. 1982. The chemistry of the Delaware Estuary. General considerations. <u>Limnol. Oceanogr.</u> 27: 1015-1028.
- Sholkovitz, E.R. 1976. Flocculation of dissolved organic carbon and inorganic matter during the mixing of river and seawater. Geochim. Cosmochim. Acta 40: 831-845.
- Smith, J. D. and Longmore, A. R. 1980. Behaviour of phosphate in estuarine water.

 Nature 287: 532-534.
- Spivakov, B. Y. A., Maryutina, T.A. and Muntau, H. 1999. Phosphorus speciation in water and sediments. <u>Pure Applied Chemistry</u> 71(11): 2161-2176.
- Stone, M. and English, M.C. 1993. Geochemical composition, phosphorus speciation and mass transport of fine-grained sediment in 2 Lake Erie tributaries.

 Hydrobiologia 253(1-3): 17-29.
- Stumm, W. and Morgan, J.J. 1996. <u>Aquatic chemistry: chemical Equilibria and Rates in Natural Waters</u>. New York: John Wiley & Sons.
- Sundby, B., Gobeil, C. Silverberg, N. and Mucci, A. 1992. The phosphorus cycle in coastal marine sediment: <u>Limnology and Oceanography</u> 37:1129-1145.
- Suzumura, M. and Koike, I. 1995. Application of soild-phase extraction technique for determination of phosphorus in sediment extract. <u>Geochemical Journal</u> 29(5): 331-335.

- Umnuay, G. 1984. The behavior of some trace elements in the Chao Phraya Estuary.

 In <u>Proceeding of the Third seminar on the water quality and Quality of Living</u>

 Resources in Thai Waters, 26-28 March, 1984, pp. 481-486. National Research

 Council of Thailand, Bangkok.
- Van Bennekom, A. J., Berger, G. W., Helder, W. and Devries, R. T. P. 1978. Nutrient Distribution in the Zaire Estuary and River Plume. <u>Neth. J. Sea Res.</u> 12: 296-323.
- Van Bennekom, A. J. and Salomon, W.1979. Pathways of nutrients and organic matter

 From land to ocean through rivers. In J.M. Martin, J.D. Burton and D. Eisma

 (eds.), River Input to Ocean Systems, Proceeding of a SCOR/ ACMRR/ECOR/

 IAHS/UNESCO/ CMG/IABO /IAPSO Review and Workshop, 26-30 March, 1979,

 pp.33-51. Rome: FAO Headquarter.
- Van Eck, G.T.M. 1982. Forms of phosphorus in particulate matter from the Holland Diep/Haringvliet, the Netherlands. <u>Hydrobiologia</u> 92: 65.
- Vink, S., Chambers, R. M., and Smith, S. V. 1997. Distribution of phosphorus in sediments From Tomales Bay, California. Marine Geology 139: 157-179.
- Wallast, R. 1983. Interactions in estuaries and coastal waters. In B. Bolin and R.B. Cook (eds.), <u>The Major Biogeochemical Cycles and Their interactions</u>, pp.385-407. New York: John Wiley and Sons.
- Walton, A. 1978. Methods for Sampling and Analysis of Marine Sediments and Dredged Materials, Ocean Dumping Report. Ottawa: RBT Printing Limited.
- Watanabe, F.S. and Oilsen, S.R. 1962. Colorimetric Determination of Phosphorus in water extracts of soil. <u>Soil Science</u> 93:183.188.
- Williams, J.D.H., Mayer, T. and Nriagu, J.O. 1980. Extractabillity of phosphorus from phosphate minerals common in soils and sediments. Soil Sci. Soc. Am. J. 44:462-465.
- Williams, J.D.H., Syers, J.K. and Walker, T.W. 1967. Fractionation of soil inorganic phosphorus a modification of Chang and Jackson's procedure. Soil. Sci. Soc. Am. Proc. 31: 736.

Windom, H.L. Silpipat, S. Changpongsang, A. Smith, R.G. and Hungspreugs, M. 1984.

Trace metal composition of and accumulation of sediment in the upper Gulf of

Thailand. Estuarine, Coastal and Shelf Science 19: 133-142.



APPENDICES

APPENDIX A

Particle size distribution analysis

Particle size distribution (PSD) of sediment samples in this study was carried out by hydrometer technique. This classical method is based on the density of settling particles suspension. The greater the density of suspension, the greater the bouyant force on the hydrometer and the higher the reading. As particles settle out of the suspension, the density decreases and a lower reading is served. Since temperature influences the settling rate, the temperature must be checked and kept constant throughout the determination. Hydrometer reading should also be corrected for the use of dispersing agent.

Apparatus

- hydrometer
- sedimentation cylinder
- Plunger
- Electric blender
- 500 ml beaker

Reagents

- 5% Calgon solution: dissolve 35.7 g of sodium hexametaphosphate and
 7.94 g of anhydrous sodium carbonate in distilled water, then dilute to 1 L.
- Amyl alcohol

Procedure

- 1. Weigh 50 g freeze-dried sediment in a 600 ml beaker.
- Add 50 ml of 5% Calgon and then add 150 ml of distilled water, mix well and stand overnight.
- Transfer the suspension into an electric blender and mix the suspension for 1-2 min.

- 4. Carefully pour the suspension into a sedimentation cylinder. Be sure to wash all of the sample into cylinder.
- 5. Add distilled water to the cylinder until the level reaches 1000 ml.
- 6. Using a plunger, stir the suspension in the cylinder up and down 20 times.
- Add 2-3 drops to 1 ml of Amyl alcohol to eliminate bubble after vertical mixing.
- 8. Remove the plunger and note the exact time.
- Carefully lower the hydrometer into the cylinder and read when
 seconds have elapsed.
- 10. Remove the hydrometer after reading. Rinse and wipe dry. This reading gives the amount of silt and clay in the sample.
- 11. Measure and record temperature of suspension.
- After the first reading, allow the cylinder to stand undisturbed for 2 hours.
- 13. Place the hydrometer in the cylinder and make the 2-hour reading. This reading indicates the amount of clay in the sample. Also measure the suspension's temperature. (Ideally the temperature should be kept constant throughout the determination).
- 14. Blank is also determined by the same method described above.
- 15. Calculate the percentage of sand, silt and clay and then determine the sediment texture by using the texture triangle (see figure A1).

Calculation

%(silt+clay) = $[(Rs - Rb) + 0.36(Ts - Tb)] \times 100$ first 40 seconds wt of sample

Rs = density of sample at first 40 seconds

Rb = density of blank at first 40 seconds

Ts = temperature of sample at first 40 seconds

Tb = temperature of blank at first 40 seconds

% Clay =
$$(Rs-Rb) + 0.36(Ts - Tb) \times 100$$

..... Next 2 hours.

wt of sample

Rs = density of sample at 2 hours

Rb = density of blank at 2 hours

Ts = temperature of sample at 2 hours

Tb = temperature of blank at 2 hours

% Silt = %(Silt + Clay) - % clay

% Sand = 100 - %(Silt +Clay)

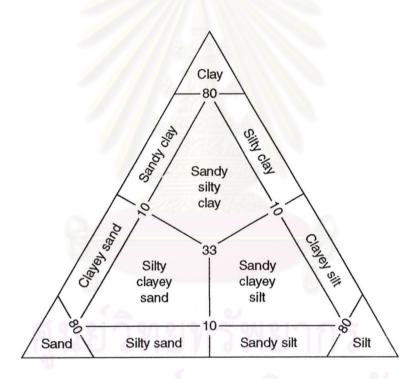


Figure A.1 Triangular classification diagram for particle size distribution (PSD) according to Gorsline (1960)

APPENDIX B

Elemental composition analysis

Elemental composition of sediment samples in this study was qualitatively and quantitatively analyzed by X-ray Fluorescence technique. This non-destructive method is based on the fact that emission of fluorescent X-ray after atom is irradiated by primary X-ray. Since fluorescent X-ray of each element has specific wavelength, this can be utilized to specify elements in sample according to Bragg's law (qualitative analysis). Furthermore, the intensity of fluorescent X-ray is also measured for quantitative analysis.

A Siemens SRS3000 sequential X-ray fluorescence spectrometer (XRF) compatible with SPECTRA3000 software is utilized in this study. This spectrometer is installed at the laboratory of the WBB Clay and Minerals company. Diagram of this X-ray unit is shown in Figure B.1. Sediment samples were prepared by fused cast bead method (according to ISO/DIS12677) before analyzing elemental composition by XRFS. Thirty-two certified reference materials were prepared by the same way as samples and used in determining calibration graphs or equations and for correction of matrix effect. Three Japanese standards of sedimentary rocks (JLK-1, JSd-1 and JSd-3) from Geological survey of Japan (1999) were analyzed as samples to check the accuracy and precision of the instrument and methodology. Loss on ignition (LOI) testing was also conducted to measure the accuracy of the analysis.

Principle of X-ray fluorescence spectrometer

According to figure B.1, samples are irradiated with primary X-ray to emit Fluorescent X-ray. The Fluorescent X-ray is then controlled to become parallel beam (by a slit of goniometer) straightforward onto the surface of a plane crystal. Then the fluorescent X-ray diffract from the plane crystal according to Bragg's law ($2d\sin\theta = n\lambda$). A detector that rotates at the same velocity of a goniometer measures the energy of the X-ray quanta (intensity of X-ray) whereas goniometer measure the reflection angle (θ and 2θ) of X-ray. The energy is then converted into electrical impulses or counts and used

in calculation of concentration of element from the equations of X-ray intensities and concentration of elements by computer software (SPECTRA3000).

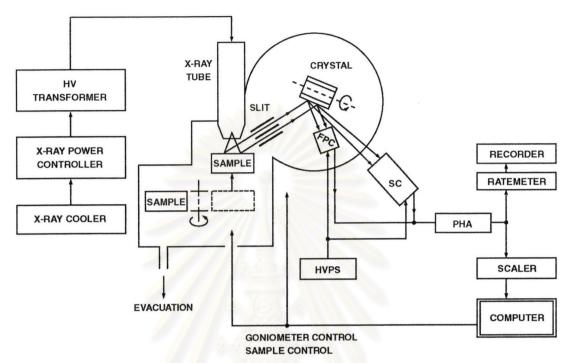


Figure B.1 Diagram off X-ray flourescence spectrometer

Preparation of sample

Sediment sample of this study were prepared by fused cast bead method according to ISO/DIS12677 (1998). The sediment powder is fused with a suitable flux to destroy its mineralogy and particulate composition.

Apparatus

- Platinum-gold crucible and lid
- Claisse Flux machine, three burner fusion system
- Vacuum dessicator
- Balance
- Oven
- Hood

Chemicals

- Lithium metaborate, Li₂B₄O₇
- Lithium Iodide, Lil

Procedure

Dry <125µm fraction sediment sample overnight in an oven at 110 °C, cool in a vacuum dessicator. 1 g of the sediment sample is weighed into a platinum-gold crucible with 5 g of pure lithium metaborate and then mix well. One drop of lithium iodide solution is added into the platinum crucible to prevent crack of glass bead after cooling down. Fuse at 1,000°C with the fluxer machine. After fused flux is poured on a platinum lid, let it cool for 5 min. Label the bead with a piece of label paper and store in a polyethylene seal-bag and then the bag should be stored in the vacuum dessicator until XRF analysis.

LOI testing

Loss on ignition (LOI) is used in estimating sediment moisture, organic matter, organic carbon, and carbonate content. LOI is considered to be an essential parameter for the XRF analysis. By ignoring LOI the total cannot be used as a measure of the accuracy of the analysis. LOI has been traditionally done by gravimetric method.

Apparatus

- Platinum crucibles
- Muffle furnace
- Balance
- Vacuum dessicator

Procedure

Weigh 2 g of dried sample into a platinum crucible. Then place the platinum crucible into a furnace. Heat at 1000°C for 4-10 h and cool it in a vacuum dessicator. Finally, weigh and calculate % of loss on ignition.

APPENDIX C

Determination of carbonate content in sediment

The acid-base titration technique (Gross, 1971) is chosen because of its simplicity and suitability. The sediment sample is treated with excess amount of standardized hydrochloric acid. Complete the reaction between acid and carbonate by heating, then back titrate the excess acid with sodium hydroxide solution using phenolphaline as an indicator.

Apparatus

- 250 ml Erlenmayer flasks
- 25 ml Burette with scale division 0.1 ml or more
- pH meter
- waterbath
- magnetic stirer and magnetic bars
- 50 ml , 100ml , 250 ml , 1000 ml volumetric flasks

Reagents

- 0.5 M HCI
- 0.25 M NaOH
- Phenolpthaline solution: dissolve 100 mg of solid 100 ml of 80 % ethanol
- Na₂CO₃
- Potassium hydrogen pthalate (KH₈H₄O₄)
- Bromocresol green solution: dissolve 0.1 g of Brocresol green in 20 % ethanol and dilute to 100 ml

Procedure

- 1. Accurately weigh 1 g of sediment sample (in this study, particle size is less than 125 μ m) and transfer to 250 ml Erlenmayber flask.
- 2. Add 10 ml of 0.5 M HCl and then heat at about 90 °C for 20 minute.

- 3. Test pH of solution with pH meter, if pH is more than 2, add another 10 ml of HCl and repeat heating for 20 minute.
- 4. When pH is less than 2, dilute the solution with 100 ml of distilled water.
- 5. Back titrate with 0.25 M NaOH using phenolphthaline as an indicator. The color will change sharply from colourless to pink at the end point. The pH meter is applied to check the end point of reaction (pH = 7) because sediment suspension will hide pink color of end point.

Standardization of 0.25 M NaOH

- Dry potassium hydrogen pthalate in an oven at 110 °C for 2 hour and cool in a dessicator.
- 2. Weigh 1.0 g of potassium hydrogen pthalate in 250 ml Erlenmayer flask
- 3. Dissolve in 100 ml of distilled water.
- 4. Add 3-4 drops of phenolphthaline.
- Titrate with 0.25 M NaOH until the pink color develops and persists for 30 seconds.
- 6. Three replicates should be done.

Standardization of 0.5 M HCI

- 1. Dry Na₂CO₃ in an oven at 110 °C for 2 hour and cool in a dessicator.
- 2. Weigh 0.6-0.7 g portion of Na₂CO₃ in a 250 ml Erlenmayer flask.
- 3. Dissolve the solid with 50 ml distilled water
- 4. Add 3-4 drops of bromocresol green
- 5. Titrate with 0.5 M HCl solution until the solution just begins to change from blue to green.
- 6. Boil the solution for 2-3 minutes, cool at room temperature and complete the tritation if the color is changed from green to blue.
- 7. Three replicates should be done.

Calculation

 $Percent \ CaCO_3 \ = [100x0.05x(ml \ HCl)(M_{HCl})] - [(ml_{NaOH})(M_{naOH})]$

APPENDIX D

Determination of readily oxidizable organic matter in sediment

The method for determination of readily oxidizable organic matter in three estuarine sediments of this study is the Walkey-Black method (1947) which adopted by Loring and Rantala (1977). The readily oxidizable organic matter in sediment is allowed to oxidize with chromic acid and the excess chromic acid is reduced by using ferrous solution. This method will not interfere other non-sensitive organic carbon like charcoal and graphite, etc. Proteins may also remain unoxidized. Since carbon only constitutes about 58 % of the soft organic remains in sediments, the carbon content can be converted to the organic matter content by multiplying the formular.

The oxidation of carbon by chromic acid may be represented as following:

$$2Cr_2O_7^{2-} + 3C + 28H^{\dagger}$$
 \longrightarrow $4Cr^{\dagger} + 3C^{4+} + 14H_2O$

and the reduction of Cr₂O₇²⁻ by ferrous solution may be given as

$$Cr_2O_7^{2-} + 6 Fe(NH_4)_2^{4+} + 14H^+ \longrightarrow 2Cr^+ + 6Fe(NH_4)^{4+} + 6 NH_4^+ + 7H_2O$$

Reagents:

- 1. 85 % phosphoric acid (H₃PO₄)
- 2. Solid sodium flouride (NaF)
- 3. Concentrated sulfuric acid (H₂SO₄)
- Silver sulfate (Ag₂SO₄)
- 5. Potassium dichromate (K₂Cr₂O₇)
- 6. Ferrous ammonium sulfate (Fe(NH₄)₂(SO₄)₂ 6H₂O)
- 7. Diphenylamine
- 8. Glucose (C₆H₁₂O₆)

Preparation of solutions:

Concentrated sulfuric acid (H₂SO₄) with silver sulfate (Ag₂SO₄)
 Dissolve 2.5 grams of silver sulfate in one litre of concentrated sulfuric acid. Store the solution in a glass-stoppered bottle.

2. Standard potassium dichromate (K₂Cr₂O₇) solution

Dissolve 49.04 grams of potassium dichromate in distilled water. Dilute the solution with distilled water to make one litre. Keep the solution in a glass-stoppered bottle.

3. 0.5 N ferrous ammonium sulfate solution

Dissolve 196.1 grams of ferrous ammonium sulfate in 800 ml of distilled water that is already filled with 20 ml of concentrated sulfuric acid. Store the solution in a glass-stoppered bottle.

4. Diphenylamine indicator

Dissolve 0.5 grams of A.R. grade diphenylamine in a mixture of 20 ml of distilled water and 100 ml of concentrated sulfuric acid. Keep the solution in a glass-stoppered bottle.

Procedure:

Approximately 0.5 grams of freeze-dried sediment is weighed out and place into a 250 ml flask. Then 10 ml of 1N $K_2Cr_2O_7$ and 20 ml of concentrated H_2SO_4 with Ag_2SO_4 are added to the sediment. The solution is then swirled and left for 30 minutes. After 30 minutes, the solution was diluted to 200 ml with distilled water. Then, 10 ml of 85 % H_3PO_4 , 0.2 grams of NaF, and 15-20 drops of diphenylamine indicator are added. The diluted solution is then back titrated with 0.5 N ferrous ammonium sulfate solution. During the process of titration, the color of the solution gradually changes from a dull green to blue and then to a brilliant green. This final color change indicates the end point.

The procedure is repeated by using 0.01 grams of glucose as the standard in order to determine the definie concentration of the 1 N $\rm K_2Cr_2O_7$ solution. The procedure was also repeated in determining a reagent blank.

Calculations:

After completing the back titration, the following calculation is made in order to determine the percentage (%) of organic matter and organic carbon in each of the sediment samples.

For sample

% organic matter = 10(1-T/S)XF

when S = the volume of 0.5 N ferrous ammonium sulfate solution used in titrating the "reagent blank"

T = the volume of 0.5 N ferrous ammonium sulfate solution used in titrating the "sediment sample"

 $F = (K_2Cr_2O_7 \text{ concentration})x(12/4000)x1.72x(10/\text{weight of the sample})$ Which 12/4000 = milliequivalent(meq.) weight of carbon 1.72 = factor for organic matter from carbon

For standard (glucose, C₆H₁₂O₆)

meq. per 100 grams = 10(1-T/S)x(100/weight of glucose)

Therefore, meq. per 1 gram = [10(1-T/S)x(100/weight of glucose)]/100

= n

then, nxmeq. per gram(12/4000) = C and, Cx100 % = % of concentration = y%

In theory, when titrated with 1 N $K_2Cr_2O_7$, the percentage of concentration should equal to 39.99 %. Therefore,

 $39.99 \% K_2Cr_2O_7$ will have a concentration of 1 N and $y\% K_2Cr_2O_7$ will have a concentration of (y%/39.99%) N

APPENDIX E

Matrix effect of extractants on standard calibration curve for phosphorus

Table E.1 Matrix effect of extractants on standard calibration curve for phosphorus
- Strickland and Parsons (1972)'s procedure.

Matrix	dilution	slope	deviation	R ²	A reagent blank
deionized water	1	0.0200	0.0000	1.0000	0.000
	1	0.0209	-0.0002	0.9999	0.000
1 M MgCl ₂	5	0.0205	-0.0008	0.9986	0.000
	5	0.0217	0.0000	1.0000	0.000
	5	0.0200	0.0000	1.0000	0.000
	10	0.0200	0.0000	1.0000	0.000
0.5 M NaCl	10	0.0200	0.0000	1.0000	0.000
1 M NaOAc	20	0.0204	-0.0002	0.9999	0.000
	20	0.0206	0.0006	0.9988	0.000
	20	0.2210	-0.0002	0.9999	0.000
1 M NaOAc+1 M MgCl ₂	1	0.0183	0.0000	1.0000	0.000
	1	0.0184	-0.0006	0.9991	0.000
	1	0.0192	-0.0002	0.9999	0.000
0.5 M HCI	20	0.0200	0.0000	1.0000	0.000
1 M HCI	10	0.0200	0.0000	1.0000	0.000
	100	0.0209	-0.0002	0.9999	0.000
	100	0.0200	0.0000	1.0000	0.000
	100	0.0206	-0.0006	0.9996	0.000
6 M HCI	30	0.0204	-0.0002	0.9999	0.000
	30	0.0205	-0.0002	0.9996	0.000
10% SDS+ 6M HCI	30	0.0205	-0.0002	0.9996	0.000
0.1 M NaOH	2	0.0209	-0.0002	0.9999	0.000
	5	0.0208	0.0002	0.9999	0.000
	10	0.0209	-0.0002	0.9999	0.000
1 M NaOH	5	0.0209	0.0008	0.9999	0.001

Table E.2 Matrix effect of extractants on standard calibration curve for phosphorus

-Koroleff (1976) 's procedure.

Matrix	dilution	slope	deviation	R ²	A reagent blank
deionized water	1	0.0230	0.0000	1.0000	0.000
	1	0.0230	0.0000	1.0000	0.000
	1	0.0230	0.0000	1.0000	0.001
1 M MgCl ₂	5	0.0239	0.0002	1.0000	0.000
	5	0.0250	0.0000	1.0000	0.000
	5	0.0230	0.0000	1.0000	0.000
	5	0.0240	-0.0008	0.9995	0.000
	5	0.0250	0.0000	1.0000	0.000
	5	0.0230	0.0000	1.0000	0.000
NaOAc	20	0.0251	-0.0002	0.9999	0.000
	20	0.0250	0.0000	0.9997	0.000
	20	0.0253	0.0005	0.9998	0.000
1 M NaOAc+1 M MgCl ₂	1	0.0208	0.0008	0.9888	0.000
	1	0.0212	-0.0006	0.9989	0.000
	1	0.0280	0.0000	1.0000	0.000
1 M HCI	10	0.0228	0.0004	0.9997	0.000
	10	0.0227	0.0002	1.0000	0.000
	10	0.0215	-0.0002	1.0000	0.000
	20	0.0225	-0.0002	1.0000	0.000
	20	0.0218	-0.0004	0.9999	0.000
	20	0.0226	0.0006	0.9999	0.000
	20	0.0229	0.0006	0.9999	0.000
	20	0.0229	0.0004	0.9999	0.000
	25	0.0228	0.0006	0.9999	0.000
	25	0.0229	0.0007	0.9998	0.000
	25	0.0228	0.0003	1.0000	0.000
	25	0.0227	0.0007	0.9999	0.000

APPENDIX F

Total phosphorus in sediments from various total analytical methods

Table F.1 Total phosphorus ($\mu g/g$ sediment) from Aspila method (Aspila et al., 1976)

Sample	Replicate	Total P	Mean ± SD	RSD	
		(µg/g sediment)	(μg/g sediment)	(%)	
Mae Klong (M)	M1	287.33			
	M2	284.60			
	МЗ	276.41			
	M4	288.07	207 00+6 69	2.33	
	M5	288.07	287.00±6.68	2.33	
	M6	282.66			
	M7	299.44			
	M8	291.32			
Chao Phraya (C)	C1	402.46			
	C2	392.26			
	C3	409.25			
	C4	390.21	200 40 40 40	1.63	
	C5	393.59	398.18±6.49	1.63	
	C6	396.98	6		
	C7	403.74			
	C8	396.98	(1)		
Bang Pakong (B)	B1	525.84			
	B2	522.24	เยากร		
	В3	522.45	524 00 10 00	1.04	
	B4	545.80	531.90±9.83	1.84	
	B5	535.61	9115 18		
	B6	539.44			

Note: each replicate was analysed three times

Table F.2 Total phosphorus ($\mu g/g$ sediment) from Modified Aspila method (Vink et al., 1997)

Sample	Replicate	Total P	Mean ± SD	RSD	
		(μg/g sediment)	(μg/g sediment)	(%)	
Mae Klong (M)	M1	359.54			
	M2	359.54	359.49±0.08	0.02	
	M3	359.40			
Chao Phraya (C)	C1	497.27			
	C2	516.87		3.16	
	C3	497.47	491.27±15.53		
	C4	478.68			
-	C5	478.68			
	C6	478.68			
Bang Pakong (B)	B1	706.62			
	B2	725.61			
	ВЗ	7.25.61	687.63±36.04	5.24	
	B4	668.63	007.00±30.04	0.24	
	B5	649.63			
	B6	649.63			

Note: each replicate was analysed three times

Table F.3 Total phosphorus ($\mu g/g$ sediment) from Agemian (1997) 's method

Sample	Replicate	Total P	Mean ± SD	RSD
6	นยว	(μg/g sediment)	(μg/g sediment)	(%)
Mae Klong (M)	M1	314.41		
0.980	M2	299.60	309.46±7.40	2.39
9 N I	МЗ	314.39	9110 18	
Chao Phraya (C)	C1	418.42		
	C2	418.50	418.47±0.04	0.009
	C3	418.50		
Bang Pakong (B)	B1	555.80		
	B2	555.68	552.41±9.03	1.63
	В3	545.76		

Note: each replicate was analysed three times

Table F.4 Total phosphorus (μ g/g sediment) from total digestion (HF-HClO₄-HNO₃) - soluble phosphate analysis by the procedure of Strickland and Parsons (1972)

Sample	Replicate	Total P	Mean ± SD	RSD
		(μg/g sediment)	(μg/g sediment)	(%)
Mae Klong (M)	M1	402.18		
	M2	397.42	394.25±8.58	2.18
	МЗ	383.14		•
Chao Phraya (C)	C1	480.33		
	C2	474.84	480.40±6.29	1.31
	C3	486.02		
Bang Pakong (B)	B1	657.79		
	B2	646.06	634.54±27.24	4.29
	ВЗ	599.53		

Note: each replicate was analysed three times

Table F.5 Total phosphorus (μg/g sediment) from total digestion (HF-HClO₄-HNO₃) - soluble phosphate analysis by the procedure of Koroleff (1976)

Sample	Replicate	Total P	Mean ± SD	RSD
		(µg/g sediment)	(μg/g sediment)	(%)
Mae Klong (M)	M1	347.52	- 31	
	M2	364.84	354.83±8.81	2.48
	МЗ	351.85		
Chao Phraya (C)	C1	506.72	101006	
[9]	C2	504.14	505.85±3.64	0.72
40	C3	506.72		/
Bang Pakong (B)	B1	648.58	2 1/8/1/8	9
9 7 1	B2	678.86	674.41±21.27	3.15
	В3	695.79		

Note: each replicate was analysed three times

APPENDIX G

Sedimentary phosphorus partitioning results by selected sequential extraction methods

Note: 1. The phosphorus partitioning results expressed in mean values \pm SD in the unit of $\mu g/g$ sediment.

- 2. The number 1, 2, 3, and 4 represent number of extraction in each fraction.
- 3. Three replicates of sediments were analyzed for phosphorus speciation.
- 4. Three replicates of sediment extract were determined for soluble phosphate.

SEDEX scheme (Ruttenberg, 1992)

Table G.1 Phosphorus partitioning in the Mae Klong estuarine sediment by SEDEX scheme (Ruttenberg, 1992)

P speciation	1	2	3	4	Total	RSD (%)
Loosely bound P	20.14 <u>+</u> 2.37	11.79 <u>+</u> 0.6	4.14 <u>+</u> 0.24	3.73 <u>+</u> 0.33	39.8 <u>+</u> 3.54	8.89
Fe-P	648.94 <u>+</u> 212.74	0.89 <u>+</u> 0.12	ND	-	649.83 <u>+</u> 212.86	32.76
Authigenic apatite	47.84 <u>+</u> 2.32	2.06 <u>+</u> 0.35	0.68 <u>+</u> 0.13	0.56 <u>+</u> 0.11	51.14 <u>+</u> 2.91	5.69
Detrital apatite+	40.93+2.63				40.93+2.63	6.43
other inorganic P	40.93 <u>+</u> 2.03		Y WASTE		40.95 <u>+</u> 2.05	0.43
Organic P	105.26 <u>+</u> 2.05	-	-		105.26 <u>+</u> 2.05	1.95
Sum of P speciation	V4				851.14 <u>+</u> 223.99	54

Table G.2 Phosphorus partitioning in the Chao Phraya estuarine sediment by SEDEX scheme (Ruttenberg, 1992)

P speciation	1	2	3	4	Total	RSD (%)	
Loosely bound P	35.41 <u>+</u> 0.38	17.09 <u>+</u> 0.32	4.33 <u>+</u> 0.06	10.69 <u>+</u> 0.45	67.52 <u>+</u> 1.21	1.79	
Fe-P	671.40 <u>+</u> 91.12	1.12 <u>+</u> 0.06	ND	np i	672.52 <u>+</u> 91.18	13.56	
Authigenic apatite	32.88 <u>+</u> 1.48	0.23 <u>+</u> 0.00	ND	ND	33.11 <u>+</u> 1.48	4.47	
Detrital apatite+	46.32+2.42	46 32+2 42	_	46.32+2.42	5.22		
other inorganic P	40.32 <u>+</u> 2.42	-	-	-	40.32 <u>+</u> 2.42	5.22	
Organic P	104.66 <u>+</u> 5.82	-	-	-	104.66 <u>+</u> 5.82	0.06	
Sum of P speciation					851.14 <u>+</u> 223.99	25	

Table G.3 Phosphorus partitioning in the Bang Pakong estuarine sediment by SEDEX scheme (Ruttenberg, 1992)

P speciation	1	2	3	4	Total	RSD (%)
Loosely bound P	22.98 <u>+</u> 0.53	21.04 <u>+</u> 0.45	4.36 <u>+</u> 0.07	12.04 <u>+</u> 0.29	60.42 <u>+</u> 1.34	2.22
Fe-P	852.38 <u>+</u> 135.77	0.88 <u>+</u> 0.07	ND	-	853.26 <u>+</u> 135.84	15.92
Authigenic apatite	27.63 <u>+</u> 1.63	3.85 <u>+</u> 0.05	0.75 <u>+</u> 0.05	0.27 <u>+</u> 0	32.5 <u>+</u> 1.73	5.32
Detrital apatite+ other inorganic P	34.73 <u>+</u> 0.87	-	<u>.</u>	-	34.73 <u>+</u> 0.87	2.51
Organic P	133.84 <u>+</u> 1.44	- 9	-	-	133.84 <u>+</u> 1.44	1.08
Sum of P speciation			1114.75 <u>+</u> 141.22	26		

Modified SEDEX scheme (Vink et al., 1997)

Table G.4 Phosphorus partitioning in the Mae Klong estuarine sediment by Modified SEDEX scheme (Vink et al., 1997)

P speciation	1	2	3	4	Total	RSD (%)
Loosely bound P	25.67 <u>+</u> 0.39	12.25 <u>+</u> 0.39	2.63 <u>+</u> 0.07	4.84 <u>+</u> 0.19	45.39 <u>+</u> 1.04	2.29
Organic P	74.06 <u>+</u> 8.16	-	-	-	74.06 <u>+</u> 8.16	11.02
Fe-P	111.74 <u>+</u> 46.78	17.16 <u>+</u> 2.29	ND	<u>-</u>	128.9 <u>+</u> 49.07	35.74
Authigenic apatite	41.78 <u>+</u> 2.25	7.75 <u>+</u> 0.5	1.81 <u>+</u> 0.32	0.91 <u>+</u> 0.14	52.25 <u>+</u> 3.21	6.14
Detrital apatite+ other inorganic P	37.72 <u>+</u> 4.71	ทยท	5:111	ปาก	37.72 <u>+</u> 4.71	12.49
Residual P	20.32 <u>+</u> 2.00				20.32 <u>+</u> 2.00	9.84
Sum of P speciation	19/1/1	36171	M.L.	7/1/21	358.64 <u>+</u> 68.19	78

Table G.5 Phosphorus partitioning in the Chao Phraya estuarine sediment by Modified SEDEX scheme (Vink et al., 1997)

P speciation	1	2	3	4	Total	RSD (%)
Loosely bound P	33.37 <u>+</u> 1.29	18.43 <u>+</u> 0.32	4.99 <u>+</u> 0.13	11.52 <u>+</u> 0.15	68.31 <u>+</u> 1.89	2.77
Organic P	77.39 <u>+</u> 5.23	-	-	-	77.39 <u>+</u> 5.23	6.76
Fe-P	81.50 <u>+</u> 0.00	23.60 <u>+</u> 1.34	ND	-	105.1 <u>+</u> 1.34	1.27
Authigenic apatite	15.66 <u>+</u> 0.89	3.76 <u>+</u> 0.21	1.18 <u>+</u> 0.15	0.29 <u>+</u> 0.12	20.89 <u>+</u> 1.37	6.56
Detrital apatite+ other inorganic P	31.68 <u>+</u> 1.92	-	· <u>-</u>	-	31.68 <u>+</u> 1.92	6.06
Residual P	16.86 <u>+</u> 4.18		-	-	16.86 <u>+</u> 4.18	24.79
Sum of P speciation	Sum of P speciation					

Table G.6 Phosphorus partitioning in the Bang Pakong estuarine sediment by Modified SEDEX scheme (Vink et al., 1997)

P speciation	1	2	3	4	Total	RSD (%)
Loosely bound P	26.78 <u>+</u> 0.40	21.87 <u>+</u> 0.34	4.86 <u>+</u> 0.13	11.88 <u>+</u> 0.16	65.39 <u>+</u> 1.03	1.58
Organic P	74.72 <u>+</u> 0.04	350	14/4-4-	-	74.72 <u>+</u> 0.04	0.03
Fe-P	202.36 <u>+</u> 123.86	23.61 <u>+</u> 2.70	ND	-6)		56.01
					225.97 <u>+</u> 126.56	
Authigenic apatite	14.59 <u>+</u> 1.40	2.60 <u>+</u> 0.15	1.16 <u>+</u> 0.00	0.33 <u>+</u> 0.00	18.68 <u>+</u> 1.55	8.30
Detrital apatite+ other inorganic P	26.35 <u>+</u> 0.78	9/1 0 1 9/1	₹ <u>0</u> 010	แกลร	26.35 <u>+</u> 0.78	2.96
Residual P	20.32 <u>+</u> 2.00	TUT	0./11	J 1.11	20.32 <u>+</u> 2.00	9.84
Sum of P speciation					431.13 <u>+</u> 131.94	79

Table G.7 Phosphorus partitioning in sediments by Agemian's extraction scheme (Agemian, 1997)

P speciation	Sediment of this study				
	Mae Klong	Chao Phraya	Bang Pakong		
Loosely sorbed P	21.70 <u>+</u> 0.00	34.79 <u>+</u> 1.37	15.50 <u>+</u> 0.00		
Fe-P	212.23 <u>+</u> 4.43	330.81 <u>+</u> 6.67	531.19 <u>+</u> 16.03		
Polyphosphate	17.27 <u>+</u> 0.82	52.05 <u>+</u> 0.89	133.80 <u>+</u> 0.00		
Calcium bound P	123.99 <u>+</u> 0.01	115.04 <u>+</u> 7.00	50.98 <u>+</u> 6.78		
Residual P	27.10 <u>+</u> 1.59	33.89 <u>+</u> 1.35	52.98 <u>+</u> 1.63		
Sum of P speciation	402.79 <u>+</u> 6.85	566.58 <u>+</u> 17.28	748.45 <u>+</u> 24.44		

Table G.8 RSD (%) of phosphorus partitioning in sediments by Agemian's extraction scheme (Agemian, 1997)

P speciation	Sediment of this study				
	Mae Klong	Chao Phraya	Bang Pakong		
Loosely sorbed P	0.00	3.94	0.00		
Fe-P	2.09	2.02	3.02		
Polyphosphate	4.78	1.71	0.00		
Calcium bound P	0.01	6.08	13.30		
Residual P	5.87	0.04	3.08		
Sum of P speciation	13	14	19		

BIOGRAPHY

Patcharee Wiratchapun was born on November 20, 1975 in Bangkok.

She graduated with a Bachelor degree of Science in 1996 from Department of Marine Science, Faculty of Science, Chulalongkorn University. After graduation, she worked as an environmental scientist for an environmental consultant company. She has continued her advance study for Master Degree at Inter-Department of Environmental Science, Chulalongkorn University.